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1 **Modelling photochemical pollutants in a deep urban street canyon:** 2 **Application of a coupled two-box model approximation**

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8 **Abstract:**

9 Air pollution associated with road transport is a major environmental issue in urban areas. Buildings
10 in urban areas are the artificial obstacles to atmospheric flow and cause reduced ventilation for
11 street canyons. For a deep street canyon, there is evidence of the formation of multiple segregated
12 vortices, which generate flow regimes such that pollutants exhibit a significant contrast between
13 these vortices. This results in poor air ventilation conditions at pedestrian level, thereby leading to
14 elevated pollutant levels and potential breaches of air quality limits. The hypothesis of a well-mixed
15 deep street canyon in the practical one-box model approach is shown to be inappropriate. This study
16 implements a simplified simulation of the canyon volume: a coupled two-box model with a reduced
17 chemical scheme to represent the key photochemical processes with timescales similar to and
18 smaller than the turbulent mixing timescale. The two-box model captures the significant pollutant
19 contrast between the lower and upper parts of a deep street canyon, particularly for NO₂. Core
20 important parameters (i.e. heterogeneity coefficient, exchange velocity and box height ratio) in the
21 two-box model approach were investigated through sensitivity tests. The two-box model results
22 identify the emission regimes and the meteorological conditions under which NO₂ in the lower
23 canyon (i.e. the region of interest for the assessment of human health effects) is in breach of air
24 quality standards. Higher NO₂ levels were observed for the cases with higher heterogeneity

coefficients (the two boxes are more segregated), with lower exchange velocities (worse ventilation conditions), or with smaller box height ratios (reduced dilution possibly due to secondary smaller eddies in the lower canyon). The performance of a one-box model using the same chemical scheme is also evaluated against the two-box model. The one-box model was found to systematically underestimate NO₂ levels compared with those in the lower box of the two-box model for all the test scenarios. This underestimation generally tends to worsen for higher heterogeneity coefficients, lower exchange velocities or smaller box height ratios. This study highlights the limitation of the assumption of homogeneity in single box models for street canyon simulation, and the inherent uncertainties that must be borne in mind to appropriately interpret such model output (in particular, that a single-box treatment will systematically underestimate NO₂ as experienced at street level).

Keywords: Air pollution; Urban street canyon; Two-box model; Dynamics; Photochemistry.

45 **1 Introduction**

46 Air pollution associated with road transport is a major environmental issue in urban areas (Murena
47 et al., 2009). A street canyon is a typical urban configuration with surrounding buildings along the
48 street (Li et al., 2008). Buildings in urban areas are the artificial obstacles to urban atmospheric
49 flow (Salim et al., 2011) and cause reduced ventilation for street canyons thereby leading to air
50 pollution levels potentially much greater than air quality objectives (Sahm et al., 2002). The most
51 fundamental geometrical model of an urban street is a single infinitely long street with buildings of
52 the same height on both sides, normally termed as the two-dimensional (2D) idealised street canyon
53 with perpendicular flow (Liu et al., 2011). The characteristics of recirculation in a 2D idealised
54 street canyon are strongly dependent upon the canyon aspect ratio (AR), which is defined as the
55 ratio of building height H to street width W . Under neutral meteorological conditions, the flow
56 patterns can be classified into three regimes (Oke, 1987): isolated roughness ($AR < 0.3$), wake
57 interference ($0.3 < AR < 0.7$) and skimming flow ($AR > 0.7$). Skimming flow representing the worst-
58 case scenario for pollutant dispersion normally occurs in regular street canyons ($0.7 < AR < 1.5$) and
59 deep street canyons ($AR > 1.5$) (Murena et al., 2009). A single primary vortex is typically formed
60 within regular street canyons (e.g. $AR = 1$) (Baker et al., 2004). However, there is evidence of
61 formation of multiple vortices within deep street canyons (e.g. Zhong et al. (2015); Li et al. (2009)),
62 which can lead to greater contrasts in vertical pollutant distributions and create even poorer
63 ventilation conditions for pollutants at the bottom of the canyon.

64 Many previous canyon modelling studies treated air pollutants as passive scalars (i.e. non-reactive
65 pollutants) in street canyons as a first-order approximation. Caton et al. (2003) suggested three
66 fundamental mechanisms that determine the concentration of a passive scalar in a 2D idealised
67 street canyon, i.e. the emission rate, the advection-diffusion within the canyon, and the turbulent
68 exchange (transfer) at the canyon roof level. For a practical application, the turbulent exchange
69 mechanism is a major research challenge as this plays the key role in controlling the pollutant
70 abundance in the street canyon (Barlow et al., 2004). This phenomenon can be represented by a

71 simplified parameter called ‘transfer velocity’ (Salizzoni et al., 2009) or ‘air ventilation rate’ (Liu
72 and Leung, 2008), herein referred to as ‘exchange velocity’ (Bright et al., 2013), which is
73 responsible for quantifying the exchange of mass between the street canyon and the overlying
74 atmospheric boundary layer. However, many emissions from vehicles are reactive, evolving
75 chemically as the air parcel is circulated inside the street canyon and exchanged with the air above
76 the rooftop. Consequently, chemical processes, alongside dispersion and transport, are expected to
77 play an important role in determining the abundance of reactive pollutants. Zhong et al. (2014)
78 employed photochemical box models to investigate the segregation effects of heterogeneous
79 emissions on ozone (O_3) levels in idealised urban street canyons and evaluate their uncertainty
80 when grid-averaged emissions were adopted. Their study provides a simple and easy approach to
81 consider the effects of both chemistry and dynamics using box models with a wide range of
82 emission scenarios, but was restricted to idealised street canyons (completely segregated) with
83 emission heterogeneity between them. Liu and Leung (2008) developed a one-box (chemistry)
84 model to study reactive pollutant dispersion in street canyons ($AR=0.5, 1, 2$), using exchange
85 velocity values derived from large-eddy simulations (LES) for different canyon ARs (Liu et al.,
86 2005). Such models are unable to reproduce the significant contrasts of pollutant concentration
87 between the lower and upper canyon regions, exacerbated in deep street canyons, since the whole
88 canyon is treated as one well-mixed box for all ARs. Li et al. (2009) found that pollutants were at
89 extremely high levels near the street level in deep street canyons. Field measurements in deep street
90 canyons (Murena and Favale (2007); Murena et al. (2008)) also indicated that pollutant
91 concentrations at pedestrian level in deep street canyons could be up to three times that in regular
92 street canyons. Murena et al. (2011) and Murena (2012) attempted to implement a simplified two-
93 box model (for passive scalars) with regard to the prediction of carbon monoxide (CO)
94 concentrations in deep street canyons. The mass transfer between the two adjacent boxes inside the
95 canyon is expressed by introducing an ‘exchange velocity’. Their study provided a useful guidance
96 for improving the performance of the street-canyon operational models, e.g. Operational Street

97 Pollution Model (OSPM) (Buckland, 1998), which might otherwise be unreliable while applied into
98 a deep street canyon since they were developed for street canyons with unity aspect ratio. CO in
99 their two-box model was effectively considered a passive scalar (a reasonable approximation as CO
100 has a long chemical lifetime (weeks) in the troposphere) and therefore no chemical processing was
101 taken into account. Zhong et al. (2015) adopted a two-box model with the incorporation of simple
102 $\text{NO}_x\text{-O}_3$ photochemistry, based on the existence of two vortices in a deep street canyon as
103 characterised typical LES simulations. Their study enabled the consideration of reactive pollutants
104 for the two-box model approach. However, only simple chemistry was considered, without the
105 consideration of the volatile organic compounds (VOCs) processing (which may result in the
106 additional conversion of nitric oxide (NO) to nitrogen dioxide (NO_2)) and production of O_3 . Zhong
107 et al. (2016) presented a comprehensive review of the recent numerical modelling studies that
108 couple the dynamics and chemistry of reactive pollutants in urban street canyons. The
109 computational fluid dynamics (CFD) modelling approach can provide high spatial and temporal
110 resolution simulations of flow and pollutant fields within street canyons (e.g. Zhong et al. (2015);
111 Bright et al. (2013); Kwak et al. (2013); Li et al. (2012)). However, they normally require a high
112 level of computational resource and substantial input information (e.g. computational domain, flow
113 characteristics, boundary conditions, and chemical schemes). As an alternative tool, the box model
114 approach is relatively simple to use and permits relatively complex chemistry to be afforded in
115 street canyon modelling such that it might provide a simpler tool to explore to air pollution issues
116 for policy makers. Such box models normally require far less computational cost than CFD models.
117 However, due to the inherent semi-empirical assumptions, box models are unable to reproduce the
118 detailed distribution of the flow or pollutant fields in street canyons.

119 The two-box models of Murena et al. (2011) and Murena (2012) for an effective passive scalar or
120 Zhong et al. (2015) with the simple $\text{NO}_x\text{-O}_3$ photochemistry have successfully captured the contrast
121 between the bulk concentration in the lower street box and that in the upper street box. The present
122 study will extend the coupled two-box model approach so that it considers both NO_x and VOCs

chemical processing under a variety of wind conditions for a wide range of emission scenarios, as a computationally efficient complement to (e.g.) full CFD simulations. The performance of a one-box model with the same chemical scheme will be evaluated compared with the more comprehensive two-box model. The methodology concerning the implementation of the two-box model with the complex chemistry is described in Section 2. Various factors affecting the performance of the two-box model are investigated and discussed in Section 3 and conclusions are presented in Section 4.

2 Framework of a coupled two-box model approximation

2.1 Model setup

In the box model approach, a well-mixed hypothesis is adopted, i.e. the air inside the box is assumed to be well-mixed. The box model is a simple approach to describe the evolution of air pollutants, which only requires low computational cost. For deep street canyons, the presence of two primary counter-rotating vortices segregates the street-canyon flow into layers with contrasting dynamical features so that pollutants exhibit a significant reduction with building height; this has been reported in the literature (Murena and Favale, 2007). In such situations, the “well-mixed” assumption tends to fail (Murena et al., 2011). Therefore, a more realistic model treatment (i.e. a two-box model) is needed to capture the vertically segregated layers with a significant concentration contrast and the communication between vortices in the deep street canyon. The deep street canyon can be divided into two boxes (conceptualised in Figure 1a) with the corresponding vortex inside each box separated by using a plane at the level of $z/H = \alpha$ (where α is the box height ratio determined by the flow structure with the street canyon). It is assumed that each vortex has sufficient intensity for the chemical species to be well-mixed within the corresponding box (Murena et al., 2011). The mathematical description of the two-box model is as follows:

$$\frac{dC_{i,L}}{dt} = -\frac{w_{t,L}}{H_L} (C_{i,L} - C_{i,U}) + E_{i,L} + \Delta S_{i,L} \quad (1)$$

$$\frac{dC_{i,U}}{dt} = \frac{w_{t,L}}{H_U} (C_{i,L} - C_{i,U}) - \frac{w_{t,U}}{H_U} (C_{i,U} - C_{i,b}) + \Delta S_{i,U} \quad (2)$$

where $C_{i,L}$ (ppb) and $C_{i,U}$ (ppb) are the concentrations of the i^{th} species in the lower and upper boxes, respectively; t (s) is the time; H_L (m) and H_U (m) are the heights of the lower and upper boxes, respectively; $w_{t,L}$ (m s^{-1}) is the exchange velocity between the lower and upper boxes, and $w_{t,U}$ (m s^{-1}) is the exchange velocity between the upper box and the overlying background atmosphere; $E_{i,L}$ (ppb s^{-1}) is the emission rates of the i^{th} species released from the lower canyon; $\Delta S_{i,L}$ (ppb s^{-1}) and $\Delta S_{i,U}$ (ppb s^{-1}) are the chemical source terms of the i^{th} species in the lower and upper boxes, respectively. A reduced chemical scheme (RCS), developed and validated by Bright et al. (2013), is adopted as the chemical mechanism in this study for the derivation of the chemical source terms to be used in Equations 1-2. The RCS includes 51 chemical species and 136 chemical reactions (Table A1 in the Appendix A). The two-box model approach without the consideration of chemistry (i.e. the chemical source terms in Equations 1-2 are zero and an effective passive (non-reactive) scalar is assumed) was initially developed and evaluated by Murena et al. (2011) and Murena (2012) based on the information from steady-state CFD simulations of deep street canyons. Subsequently, the two-box model approach considering simple $\text{NO}_x\text{-O}_3$ photochemistry (i.e. the chemical source terms in Equations 1-2 are derived from simple $\text{NO}_x\text{-O}_3$ photochemistry) was implemented by Zhong et al. (2015) based on the LES simulations of two vortices formed within a deep street canyon. These previous studies provide confidence that the simulated dynamics (exchange velocities) adopted for the street canyon boxes is reasonable although ideally such box models would be tested against observations (but these are as yet very scarce). This study attempts to extend the application of two-box model approach by considering relatively more complex chemistry (i.e. the RCS chemical mechanism).

The one-box model (with the “well-mixed” assumption for the whole deep street canyon) is conceptualised in Figure 1b and formulated below:

$$\frac{d}{dt}C_{i,0}(t) = E_{i,0} - \frac{w_{t,0}}{H_0}(C_{i,0} - C_{i,b}) + \Delta S_{i,0} \quad (3)$$

where the symbols are similar to those in the two-box model (the quantities associated are denoted as “0” rather than the “U” and “L” in the two-box model approach).

We assume that $C_{i,L}$ from the more sophisticated and realistic two-box model is the “true” value (in the sense that $C_{i,L}$ is closer to the true value in comparison with $C_{i,0}$ from the one-box model). Thus, there will be an error for the “one-box” model due to the well-mixed assumption, compared with the concentration in the lower box (i.e. the interest area of potential exposure assessment for pedestrians) by the “two-box” model. This error can be expressed as the concentration difference due to segregation as follows:

$$\Delta C_{i,L} = C_{i,0} - C_{i,L} \quad (4)$$

Then we can define the percentage of overestimation by the “one-box” model compared with the concentration in the lower box by the “two-box” model:

$$\phi_{i,L}(t) = \frac{\Delta C_{i,L}(t)}{C_{i,L}(t)} \times 100\% \quad (5)$$

If $\phi_{i,L}(t) = 0\%$, it means that the “one-box” model is in agreement with the “two-box” model; If $\phi_{i,L}(t) > 0\%$ or $\phi_{i,L}(t) < 0\%$, it means that the “one-box” model over- or under-estimates the concentration compared with the “two-box” model.

2.2 Exchange velocities in the two-box model

Exchange velocities implemented into the two-box model can be determined from a comprehensive numerical flow model (e.g. the Reynolds-Averaged Navier-Stokes model or large-eddy simulation) by calculating the ventilation of a passive scalar once the boundaries of the two boxes are defined. According to Fick’s law, the flux of a passive scalar (denoted as “ps”), F_{ps} (ppb m s⁻¹), between

191 the lower and upper boxes under the steady state (the “two-box” model approach) can be written as
 192 follows,

$$193 \quad F_{ps} = w_{t,L}(C_{ps,L} - C_{ps,U}) \quad (6)$$

194 Similarly, the flux between the upper box and the background air under the steady state must be
 195 equal to the flux in (6) and it can be expressed as:

$$196 \quad F_{ps} = w_{t,U}(C_{ps,U} - C_{ps,b}) \quad (7)$$

197 If the whole street canyon is considered as one box, the flux of a passive scalar for the whole box
 198 under the steady state (one-box model approach) is derived as:

$$199 \quad F_{ps} = w_{t,0}(C_{ps,0} - C_{ps,b}) \quad (8)$$

200 We should also have the following equation due to the definitions of the three concentrations and
 201 the volumes of the boxes:

$$202 \quad C_{ps,0} = \alpha C_{ps,L} + (1 - \alpha)C_{ps,U} \quad (9)$$

203 Equation 9 can be rewritten as:

$$204 \quad C_{ps,0} = C_{ps,U} + \alpha(C_{ps,L} - C_{ps,U}) \quad (10)$$

205 Here, $\alpha \in (0,1)$ is the ratio of the lower box’s volume to the volume of the whole canyon. When an
 206 idealised street canyon is considered, α becomes the box height ratio, H_L/H_0 . H_L can be determined
 207 by the flow structure within the street canyon, namely, the height of the lower vortex.

208 In this study, it is assumed that $C_{ps,b} = 0$, i.e. ‘zero background’ is assumed for a passive scalar (e.g.
 209 Murena et al. (2011) ; Murena (2012); Zhong et al. (2015)). According to Equations 7 and 8, it can
 210 be derived that $\frac{w_{t,0}}{w_{t,U}} = \frac{C_{ps,U}}{C_{ps,0}}$, which denotes the ratio of the upper canyon concentration ($C_{ps,U}$) to

211 the whole canyon averaged concentration ($C_{ps,0}$) and represents the deviation from the homogenous
 212 system (assuming the whole canyon as a well-mixed box). It is also assumed that $C_{ps,L} \geq C_{ps,U}$ is
 213 the case for passive scalars emitted from street canyons near the ground level (Figure 2). According
 214 to Equation 10, $C_{ps,0} \geq C_{ps,U}$ and $w_{t,0} \leq w_{t,U}$ can be derived. Then we may also define a non-
 215 dimensional parameter to represent the heterogeneity coefficient (or spatial variation) across the two
 216 boxes, i.e.

$$217 \quad \eta = 1 - \frac{w_{t,0}}{w_{t,U}} \quad (11)$$

218 where $\eta \in [0,1]$. If $\eta = 0$, then $w_{t,0} = w_{t,U}$ from Equation **Error! Reference source not found.** and
 219 it yields $C_{ps,0} = C_{ps,U}$ according to Equations 7 and 8, and $C_{ps,U} = C_{ps,L}$ based on Equation 10.
 220 Thus, the two boxes are homogenous. Higher (or lower) values of η represent the two boxes that
 221 are more (or less) segregated; in other words, the simulation possesses more (or less) heterogeneity.
 222 According to Equations 6-9, it can be derived that:

$$223 \quad \frac{1}{w_{t,0}} = \frac{\alpha}{w_{t,L}} + \frac{1}{w_{t,U}} \quad (12)$$

224 Based on Equations 6-12, exchange velocities for the two-box model are obtained as follows:

$$225 \quad w_{t,U} = \frac{w_{t,0}}{(1-\eta)} \quad (13)$$

$$226 \quad w_{t,L} = \frac{\alpha w_{t,0}}{\eta} \quad (14)$$

227 The physical mechanisms that determine the value of the heterogeneity coefficient (η) are explained
 228 below. For a given α (i.e. fixed sizes of the two vortices), the heterogeneity coefficient may be
 229 determined by the spatial pattern of turbulence, which could in turn be affected by the building

230 geometry, local wind conditions, local turbulence generated by moving vehicles or thermal forcing,
231 and damped turbulence by (e.g.) tree leaf or stable atmosphere factors. For example, greater local
232 vehicle generated turbulence (or other factors) transfers more pollutants from the lower box into the
233 upper box, giving a lower value of $C_{ps,L}$ and a higher value of $C_{ps,U}$. Based on Equation 7, a lower
234 value of $w_{t,U}$ is yielded. Then a lower value of η is obtained based on Equation **Error! Reference**
235 **source not found.**; namely, the two-box system possesses less heterogeneity. If only the wind
236 speed above the canyon is considered and the exchange velocity is assumed to be scaled with the
237 wind speed (Murena et al. (2011) and Murena (2012)) for a given building geometry, η would
238 remain unchanged (i.e. the ratio of exchange velocities in Equation 11 remains unchanged). Value
239 of η may vary with the AR of the canyon, i.e. a larger AR (deeper canyon) may give a higher value
240 of η due to the worse ventilation conditions. Also, lower turbulence caused by a stable atmosphere
241 (Ramamurthy et al., 2007) and decoupling caused by an elevated tree-leaf canopy (Gromke and
242 Ruck, 2012) may give higher values of η .

243 2.3 Model Scenarios

244 Table 1 gives an overview of the case settings. For the BASE case, these parameters are set as:
245 $\eta = 0.5$, $w_{t,0} = 0.02 \text{ m s}^{-1}$ and $\alpha = 0.5$, which represent a typical urban scenario. The value of
246 $\eta = 0.5$ represents a median level of heterogeneity, i.e. the pollutant concentration in the lower (or
247 upper) box is 50% higher (or lower) than the mean concentration averaged over the whole canyon
248 for a given \mathcal{A} of 0.5. In other words, the concentration in the lower box is 3 times that in the upper
249 box, which could be the case for deep street canyons (Murena and Favale (2007); Murena et al.
250 (2008)). The value for $w_{t,0} = 0.02 \text{ m s}^{-1}$ is used based on those derived from large-eddy simulations
251 for street canyons (e.g. Zhong et al. (2015); Bright et al. (2013)) while the reference incoming wind
252 speed is about 2 m s^{-1} . This investigation is focused on highly polluted scenarios, i.e. calm wind
253 blowing across the street canyon rather than windy conditions. $w_{t,0}$ is assumed to scale with the
254 reference wind speed above the street canyon (Murena et al. (2011) and Murena (2012)) while

255 keeping the same turbulence pattern. The value of $\alpha = 0.5$ represents equal size vortices (volume of
 256 air) for both lower and upper boxes (e.g. found in the CFD study by Kwak et al. (2013)), which
 257 represents a typical situation for deep street canyons. To investigate the effect of η , the values of
 258 other parameters are assumed to kept the same as those used in Case BASE and a series of values of
 259 η are considered, i.e. Case HC-LL ($h = 0.1$), Case HC-L ($\eta = 0.3$), Case HC-H ($\eta = 0.7$) and Case
 260 HC-HH ($\eta = 0.9$). Likewise, a series of other cases together with their parameters are also
 261 summarised in Table 1, i.e. the effect of varying $w_{t,0}$ with Case EX-LL ($w_{t,0} = 0.012 \text{ m s}^{-1}$), Case
 262 EX-L ($w_{t,0} = 0.016 \text{ m s}^{-1}$), Case EX-H ($w_{t,0} = 0.024 \text{ m s}^{-1}$) and Case EX-HH ($w_{t,0} = 0.028 \text{ m s}^{-1}$);
 263 and the effect of varying a with Case HB-LL ($a = 0.1$), Case HB-L ($a = 0.3$), Case HB-H ($a = 0.7$),
 264 and Case HB-HH ($a = 0.9$). As both η and α range from 0 to 1, our tests of (0.1, 0.9) for both
 265 parameters covers a wide range of most possible scenarios. Our tests of (0.012, 0.028) m s^{-1} for the
 266 exchange velocity are mainly focus on the sensitivity to this typical situation (0.02 m s^{-1} for Case
 267 BASE). For each case, the corresponding ‘one-box’ model and the ‘two-box’ model were run
 268 (Figure 1). Figure 3 illustrated the exchange velocities (based on Equations 13-14) implemented in
 269 the ‘two-box’ model for the scenarios in Table 1, considering the effect of η , $w_{t,0}$ and a ,
 270 respectively. Figure 3a shows that, for a given $\alpha = 0.5$ and $w_{t,0} = 0.02 \text{ m s}^{-1}$, as η increases, $w_{t,L}$
 271 increases, but $w_{t,U}$ decreases. Figure 3b shows that, for a given $\alpha = 0.5$ and $\eta = 0.5$, as $w_{t,0}$
 272 increases, both $w_{t,L}$ and $w_{t,U}$ increases linearly. This linear relationship is also found in the
 273 literature (Murena et al., 2011). Figure 3c shows that, for a given $\eta = 0.5$ and $w_{t,0} = 0.02 \text{ (m s}^{-1}\text{)}$, as
 274 α increases, $w_{t,L}$ remains the same level, but $w_{t,U}$ increases linearly.

275 For each case (listed in Table 1), the corresponding ‘one-box’ model and the ‘two-box’ model were
 276 run (Figure 1). Initial and background conditions of chemistry used in this study follow those of
 277 Zhong et al. (2014), in which the independent photochemical box model is initially spun up to allow
 278 concentrations of all 51 species in RCS to be calculated. In order to characterise a wide range of

279 real scenarios, the representative E_{NOx} and E_{VOCs} are scaled by different factors of between 0.1 and 2
280 applied to those of the “Typical Real-world Emission Scenario” (TRES) (i.e. 620, 128 and 1356 g
281 $km^{-1} hr^{-1}$ for emission rates for NO_x , VOCs and CO, respectively) (Zhong et al., 2014), which
282 represents an urban continuous road traffic of 1500 vehicles h^{-1} with an average speed of 30 mph
283 and a vehicle fleet composition for the UK in the year 2010.

284 The lower street canyon is the volume of interest for the assessment of human health effects (i.e.
285 where exposure occurs). NO_2 is an important photochemical pollutant and the issue of NO_2 air
286 pollution has become an urgent agenda for the urban air quality management (Defra, 2015). This
287 article will focus on the effects of η (heterogeneity coefficient) and $w_{t,0}$ (exchange velocity), and
288 α (box height ratio) on the NO_2 characteristics in the lower canyon (box), once photochemical box
289 models have reached a quasi-steady state. The coupled two-box model represents the key
290 photochemical processes with timescales similar to and smaller than the turbulent mixing timescale
291 in street canyons. The typical time scale for the street canyon air to exchange with the external flow
292 aloft is $H_0 / w_{t,0}$, which is an order of 10 min (Bright et al. (2013)). Although the chemistry system
293 is complex and highly nonlinear, possessing a wide range of chemical time scales, the box model
294 will eventually achieve a quasi-steady state (pollutants remain nearly constants) as the run time is
295 much larger than the exchange timescale, leaving those slow chemical reactions still slightly
296 ‘unsteady’ (Bright et al. (2013)).

297 **3 Results and discussion**

298 **3.1 Effect of the heterogeneity coefficient**

299 Figure 4 illustrates the effect of the heterogeneity coefficient (η) on $C_{NO_2,L}$ (ppb), i.e. the NO_2
300 concentration in the lower box, for (a) Case HC-LL ($\eta=0.1$), (b) Case HC-L ($\eta=0.3$), (c) Case
301 BASE ($\eta=0.5$), (d) Case HC-H ($\eta=0.7$), (e) Case HC-HH ($\eta=0.9$) and (f) Selected lines for
302 analysis. In Figure 4, E_{VOCs} and E_{NOx} are normalised to the corresponding values in the “Typical

303 Real-world Emission Scenario” (TRES, represented by \triangle), derived from the fleet composition for
 304 the year 2010. The trajectory 2005-2020 shown in Figure 4 (line on each panel) represents the
 305 changing emission scenarios for 2005 to 2020, derived from the UK fleet composition projections
 306 (NAEI, 2003) and the UK Road Vehicle Emission Factors (Boulter et al., 2009) assuming constant
 307 traffic volumes and speeds equal to those in the ‘TRES’ scenario for 2010 - i.e. only the emission
 308 change with vehicle technology and fleet composition is considered, rather than traffic growth. The
 309 solid red curves highlight the UK air quality standard for hourly NO_2 (105 ppb) (no exceedances
 310 more than 18 times a year) (Defra, 2008). It is interesting to note that $C_{\text{NO}_2,L}$ generally has a similar
 311 pattern for the cases and increases with the heterogeneity coefficient from 0.1 (Figure 4a) to 0.9
 312 (Figure 4e). This can be explained by the reducing exchange between the lower and upper box
 313 (indicated by a lower value of $w_{t,L}$ when η is large in Figure 3a). The higher heterogeneity
 314 coefficient may also be considered to reflect less local traffic produced turbulence in the lower box,
 315 as this would reduce the air ventilation from the lower box to the upper box. This is consistent with
 316 the finding by Murena et al. (2011) that there would be a lower exchange velocity between the
 317 lower and upper box and a higher level of pollutant concentration in the lower box for the case
 318 without considering the local traffic produced turbulence. This indicates that heterogeneity in the
 319 street canyon significantly affects pollutant concentrations in the lower box. Therefore, it is not
 320 surprising that the solid red curve shifts from the higher emission region to the lower emission
 321 region as the heterogeneity coefficient increases (Figure 4a-e). The curve shift (or more generally,
 322 the pattern shift) is not linear, mainly due to the highly non-linear chemical regimes. It is also noted
 323 that emissions at the TRES level are expected to lead to NO_2 concentrations in breach of the UK air
 324 quality standard for hourly NO_2 , for this idealised scenario, while the heterogeneity coefficient is
 325 larger than 0.5 (Figure 4c-e). It is observed that trajectory 2005-2020 cuts across the solid red curve.
 326 This indicates the importance of future technology in the expected reduction of NO_2 levels thereby
 327 meeting the UK NO_2 air quality standards over years (although we note that such anticipated
 328 reduction may not be fully realised (Carslaw and Rhys-Tyler, 2013)). For a heterogeneity

329 coefficient of 0.9, the UK air quality standard for hourly NO_2 is breached for most years, for this
330 idealised scenario. This indicates that it is important to improve the air ventilation within the street
331 canyon, thereby decreasing the heterogeneity coefficient leading to better air quality and reduced
332 pedestrian exposure.

333 Figure 5 shows the transects of $C_{\text{NO}_2,L}$ (ppb) for Case HC-LL, Case HC-L, Case BASE, Case HC-H
334 and Case HC-HH through the selected lines for analysis in Figure 4f. The dashed line in Figure 4f
335 (“Fixed E_{NO_x} ”) represents a technology change targeting only E_{VOCs} from vehicles, or roads with a
336 varying coverage of vegetation which may emit further VOCs into the urban canopy (Loughner et
337 al., 2012). The dotted line in Figure 4f (“Fixed E_{VOCs} ”) represents a technology change targeting
338 only E_{NO_x} from vehicles. The dot-dash line in Figure 4f (“TRES-2010”) represents a technology of
339 both E_{VOCs} and E_{NO_x} with the proportional change in traffic emissions of both VOCs and NO_x from
340 vehicles specified for the TRES. This dot-dashed line may also represent control of the number of
341 vehicles in streets or scenarios for different areas (busier or less busy roads) with the same fleet
342 composition as the TRES. The trajectory line (“Trajectory 2005-2020”) indicates emission
343 scenarios for the years 2005 to 2020 with the same traffic volume and speed as the TRES. The
344 corresponding results along the selected lines are analysed below.

345 Figure 5a shows that $C_{\text{NO}_2,L}$ gradually increases with the increase of E_{VOCs} at a fixed E_{NO_x} (same as
346 that of TRES). This can be explained as VOC-derived peroxy radicals can play a key role in the
347 conversion of NO to NO_2 through chemistry; in other words, for the fixed E_{NO_x} , the increase of
348 $C_{\text{NO}_2,L}$ is mainly due to the chemical processing through VOCs. This indicates that all other factors
349 being equal, slightly higher levels of NO_2 will slightly result from more green (i.e. vegetated) areas
350 producing extra E_{VOCs} . However, this neglects the depositional loss of NO_2 to vegetation (Pugh et
351 al., 2012). It is noted that the concentration difference of $C_{\text{NO}_2,L}$ between Case HC-HH ($\eta=0.9$) and
352 Case HC-LL ($\eta=0.1$) gradually increases with the increase of E_{VOCs} , from 23 ppb (at
353 $E_{\text{VOCs}} / E_{\text{TRES,VOCs}}=0.1$) to 80 ppb (at $E_{\text{VOCs}} / E_{\text{TRES,VOCs}}=2$). This finding indicates that the effect of

354 the heterogeneity coefficient is more significant for higher E_{VOCs} when keeping E_{NOx} unchanged.
 355 Figure 5b shows that $C_{NO_2,L}$ generally increases with the increase of E_{NOx} at a fixed E_{VOCs} (same as
 356 that of TRES), with a rapid increase while $E_{NOx} / E_{TRES,NOx}$ ranges from 0.1 to 0.5. This is mainly
 357 attributed to the fact that the emitted NO_x contributes directly to the increase of $C_{NO_2,L}$. This
 358 indicates that adoption of technology controlling NO_x will have a significant effect in reducing NO_2
 359 levels (as would be anticipated). The direct contributions of NO_x emissions to $C_{NO_2,L}$ (assuming no
 360 photochemical processes) for cases with different heterogeneity coefficients are indicated by a
 361 series of radiating lines in Figure 5b. Any deviation from these radiating lines can be attributed to
 362 the contributions from photochemical processes (which convert NO to NO_2). It can be seen from
 363 Figure 5b that the chemically induced NO_2 increases rapidly for smaller E_{NOx} and becomes steady
 364 for larger E_{NOx} . It is found that the contributions from photochemistry / ozone titration are dominant
 365 over those from direct emissions, highlighting the importance of photochemistry in converting NO
 366 to NO_2 for the street canyon environment. There is also clear evidence of the reduced impact of the
 367 heterogeneity coefficient at lower E_{NOx} . The concentration difference of $C_{NO_2,L}$ between Case HC-
 368 HH and Case HC-LL gradually increases with the increase of E_{NOx} , from 13 ppb (at $E_{NOx} / E_{TRES,NOx}$
 369 =0.1) to 60 ppb (at $E_{NOx} / E_{TRES,NOx} =2$). Figure 5c illustrates the change of $C_{NO_2,L}$ for TRES-2010
 370 with changing traffic volume only (i.e. E_{VOCs} and E_{NOx} varies proportionally). The pattern of $C_{NO_2,L}$
 371 is a combination of those in Figure 5a and Figure 5b, and a nearly linear relationship is observed.
 372 This indicates that controlling the number of vehicles in street canyons with the same fleet
 373 composition as the TRES will have an approximately linear effect on the NO_2 levels. This evidence
 374 may be used to derive a simple parameterisation scheme for NO_2 with respect to traffic volume.
 375 Figure 5d shows the results of $C_{NO_2,L}$ from the year 2005 to 2020. It is observed that $C_{NO_2,L}$
 376 decreases with year. This is mainly attributed to the predicted performance of control technologies
 377 applied, which achieve lower E_{VOCs} and E_{NOx} . $C_{NO_2,L}$ begins to attain the air quality standard for
 378 hourly NO_2 (for this idealised scenario) from the year 2007 for Case HC-LL ($\eta=0.1$), 2009 for

379 Case HC-L ($\eta=0.3$), 2011 for Case BASE ($\eta=0.5$), 2014 for Case HC-H ($\eta=0.7$) and 2017 for
380 Case HC-HH ($\eta=0.9$). $C_{NO_2,L}$ represents the mean concentration of the entire lower box which may
381 still be substantially lower than the highest concentration in the hotspots near the exhaust zone
382 (Zhong et al., 2015).

383 Figure 6 shows the effect of the heterogeneity coefficient (η) on $\phi_{NO_2,L}$ (%), i.e. the percentage of
384 overestimation for NO₂ in the lower canyon, by the ‘one-box’ model, compared with the more
385 sophisticated coupled-two-box model approach. Negative values of $\phi_{NO_2,L}$ are observed for all the
386 cases. It is interesting to notice that the magnitude of $\phi_{NO_2,L}$ gradually increases with the increase of
387 heterogeneity coefficient (η), i.e. the range of (-9.54 %, -4.13 %) among all tested emission
388 scenarios for Case HC-LL with $\eta=0.1$ (Figure 6a), (-23.94 %, -11.36 %) for Case HC-L with
389 $\eta=0.3$ (Figure 6b), (-33.49 %, -17.07 %) for Case BASE with $\eta=0.5$ (Figure 6c), (-40.74 %, -
390 21.94 %) for Case HC-H with $\eta=0.7$ (Figure 6d) and (-46.73 %, -26.22 %) for Case HC-HH with
391 $\eta=0.9$ (Figure 6e). It is also noted that $\phi_{NO_2,L}$ changes nonlinearly with the change of emissions of
392 NO_x and VOCs, which is mainly attributed to nonlinear photochemical reactions. This indicates that
393 for higher VOCs emission rate scenarios (Figure 6), nonlinear photochemistry plays a key role in
394 reducing the percentage of overestimation for NO₂ by the ‘one-box’ model compared with that for
395 e.g. a passive scalar.

396 Figure 7 illustrates the transects of $\phi_{NO_2,L}$ (ppb) for Case HC-LL, Case HC-L, Case BASE, Case
397 HC-H and Case HC-HH through the selected lines for analysis in Figure 4f. Figure 7a shows that
398 the magnitude of $\phi_{NO_2,L}$ slightly increases with the increase of E_{VOCs} , i.e. from -4.48 % to -4.59 %
399 for $\eta=0.1$, from -11.88 % to -14.26 % for $\eta=0.3$, from -18.14% to -24.16 % for $\eta=0.5$, from -
400 23.57 % to -33.54 % for $\eta=0.7$ and from -28.37 % to -41.88 % for $\eta=0.9$. It is noted that the
401 higher the value of heterogeneity coefficient, the larger the magnitude of $\phi_{NO_2,L}$. This indicates that
402 the one box model performance is better for the case with lower heterogeneity coefficients or for

403 lower VOC emissions (or less “green”) areas. Figure 7b shows that the magnitude of $\phi_{NO_2,L}$
 404 generally decreases with the increase of E_{NO_x} , except for a slight increase at $E_{NO_x} / E_{TRES,NO_x} = 0.2$ for
 405 the cases with $\eta = 0.5$, $\eta = 0.7$ and $\eta = 0.9$. This may be attributed to the complexity of the nonlinear
 406 photochemistry in such segregated street canyon environment. Figure 7c also shows that there is no
 407 significant change in the $\phi_{NO_2,L}$ when changing both E_{VOCs} and E_{NO_x} and that the values of $\phi_{NO_2,L}$ are
 408 principally affected by the heterogeneity coefficient (η). This finding is also indicated by Figure 7d,
 409 in which the values of $\phi_{NO_2,L}$ do not change significantly over the simulated emissions evolution for
 410 the years 2005 to 2020 (the maximum difference is within 5 %) and there is significant contrast
 411 between the cases with a difference in heterogeneity coefficient (the contrast is around 10 % for the
 412 interval of $\eta = 0.2$).

413 **3.2 Effect of the exchange velocity**

414 Figure 8 illustrates the effect of the exchange velocity ($w_{t,0}$) on $C_{NO_2,L}$ (ppb), i.e. the concentration
 415 in the lower box, for (a) Case EX-LL ($w_{t,0} = 0.012 \text{ m s}^{-1}$), (b) Case EX-L ($w_{t,0} = 0.016 \text{ m s}^{-1}$), (c)
 416 Case BASE ($w_{t,0} = 0.02 \text{ m s}^{-1}$), (d) Case EX-H ($w_{t,0} = 0.024 \text{ m s}^{-1}$) and (e) Case EX-HH ($w_{t,0}$
 417 $= 0.028 \text{ m s}^{-1}$). $w_{t,0}$ has a direct effect on the pollutant concentration in the one-box homogenous
 418 system (also representing the whole canyon averaged pollutant concentration in the two-box system)
 419 and plays an important role in determining the lower canyon pollutant concentration in the two box
 420 system for given scenario conditions (Section 2). $w_{t,0}$ can vary with the external wind turbulence
 421 above the street canyon, the street canyon geometry and the stability of the atmosphere. It is
 422 observed that $C_{NO_2,L}$ is significantly influenced by $w_{t,0}$. For Case EX-LL, levels of $C_{NO_2,L}$ are
 423 extremely high (the maximum value could be up to 350 ppb). This corresponds to the lowest $w_{t,0}$
 424 adopted in Case EX-LL, which gives the worst (lowest) exchange between the lower and upper box
 425 (indicated by a lower value of $w_{t,L}$ in Figure 3). Therefore, pollutants are not efficiently carried
 426 from the lower box to the overlying canopy layer. It is interesting to notice that the solid red curve

427 (representing the UK air quality standard for hourly NO_2) shifts from the region with lower
428 emissions to that with higher emissions as $w_{t,0}$ increases. This means that even low emissions
429 under the worst dispersion conditions can result in very poor air quality inside street canyons. It is
430 also observed that trajectory 2005-2020 falls entirely into the region representing a breach of the
431 UK air quality standard for hourly NO_2 for Case EX-LL with the lowest $w_{t,0}$, for this idealised
432 scenario. With the increase of the exchange velocity, the solid red curve moves from the year 2020
433 towards the year 2005. It is also noted that TRES is in the region breaching the UK air quality
434 standard for hourly NO_2 for Case EX-LL, Case EX-L and Case BASE, but is within the air quality
435 limit for Case EX-H and Case EX-HH. The detailed results along the selected lines for analysis,
436 shown as Figure 4f, are presented below.

437 Figure 9 shows the transects of $C_{\text{NO}_2,L}$ (ppb) for Case EX -LL, Case EX-L, Case BASE, Case EX-H
438 and Case EX-HH through the selected lines for analysis as shown in Figure 4f. It is also observed
439 that $C_{\text{NO}_2,L}$ increases with the increase in E_{VOCs} and E_{NO_x} , shown as Figure 9a-c. This indicates that
440 the control of either E_{VOCs} or E_{NO_x} is effective to reduce the NO_2 levels, in the former case via
441 repartitioning of NO_x . It is also interesting to notice that there is less change of $C_{\text{NO}_2,L}$ where E_{VOCs}
442 is lower. The minimum and maximum differences of $C_{\text{NO}_2,L}$ between Case EX-LL with $w_{t,0}=0.012$
443 m s^{-1} and Case EX -HH with $w_{t,0}=0.028 \text{ m s}^{-1}$ are 44 ppb and 201 ppb for Figure 9a, 15 ppb and
444 136 ppb for Figure 9b, and 17 ppb and 228 ppb for Figure 9c. This indicates the importance of
445 controlling ventilation conditions of street canyons especially for highly polluted scenarios. The
446 direct contributions of NO_x emissions to $C_{\text{NO}_2,L}$ for cases with different exchange velocities are
447 represented by a series of radiating lines in Figure 9b, which indicates that photochemical processes
448 (primarily ozone titration) contribute more to NO_2 than direct emissions. It is also found that the
449 chemically induced NO_2 increases rapidly for smaller E_{NO_x} and becomes negligible for larger E_{NO_x} ,
450 due to the limited ozone supply Figure 9d shows that $C_{\text{NO}_2,L}$ decreases significantly with year due to
451 the (predicted) influence of vehicle control technologies upon both E_{VOCs} and E_{NO_x} . This indicates

452 that the air quality will be improved in future years. However, for the worst ventilation condition
453 (e.g. Case EX-LL), $C_{NO_2,L}$ is still in the breach of the UK air quality standard for hourly NO₂ over
454 the year 2005 to 2020. This indicates that control of air ventilation together with control of vehicle
455 emissions is important in improving air quality within street canyons. Air ventilation is strongly
456 influenced by the urban street design and deep street canyons could lead to poor ventilation.

457 Figure 10 shows the effect of the exchange velocity ($w_{t,0}$) on $\phi_{NO_2,L}$ (%), i.e. the percentage of
458 overestimation for NO₂ in the lower canyon by the ‘one-box’ model, compared with the two-box
459 system. It is found that $\phi_{NO_2,L}$ decreases slightly with increasing exchange velocity ($w_{t,0}$), i.e. the
460 range of (-37.49 %, -17.64 %) among all tested emission scenarios for Case EX-LL (-35.26 %, -
461 17.22 %) for Case EX-L, (-33.49 %, -17.07 %) for Case BASE, (-31.89 %, -17.02 %) for Case EX-
462 H and (-30.52 %, -17.01 %) for Case EX-HH. As $\eta = 0.5$ is adopted for all cases in Figure 10, the
463 nonlinear patterns reflect the characteristics of scenarios with a single heterogeneity coefficient.
464 This indicates that there is a systematic underestimation of NO₂ concentrations by the ‘one-box’
465 model and this underestimation changes significantly with the heterogeneity coefficient (Figure 4),
466 to a much greater extent than the change with the exchange velocity (Figure 10).

467 Figure 11 illustrates the transects of $\phi_{NO_2,L}$ (ppb) for Case EX -LL, Case EX-L, Case BASE, Case
468 EX-H and Case EX-HH through the selected lines for analysis in Figure 4f. Figure 11a shows that
469 $\phi_{NO_2,L}$ decreases modestly with the increase of E_{VOCs} , i.e. from -21.15 % to -26.86 % for Case EX-
470 LL, from -19.26 % to -25.37 % for Case EX-L, from -18.14 % to -24.16 % for Case BASE, from -
471 17.48 % to -23.16 % for Case EX-H and from -17.15 % to -22.36 % for Case EX-HH. Figure 11b
472 shows that $\phi_{NO_2,L}$ generally increases with the increase of E_{NOx} , except a slight decrease at
473 $E_{NOx} / E_{TRES,NOx} = 0.2$. Figure 11c shows that there is no significant difference between the cases
474 with different exchange velocities (within 5 %) while both E_{VOCs} and E_{NOx} are below half of those

475 for TRES. For the emission predictions corresponding to the years 2005 to 2020 shown as Figure
476 11d, there is also no significant change of $\phi_{NO_2,L}$ (within 5 % difference).

477 **3.3 Effect of the box height ratio**

478 Figure 12 illustrates the effect of the box height ratio (α) on $C_{NO_2,L}$ (ppb), i.e. the concentration in
479 the lower box, for Case HB-LL ($\alpha = 0.1$), (b) Case HB-L ($\alpha = 0.3$), (c) Case BASE ($\alpha = 0.5$), (d)
480 Case HB-H ($\alpha = 0.7$), and (e) Case HB-HH ($\alpha = 0.9$). The value of α can vary with the flow
481 structure in a street canyon, which may be significantly influenced by the building geometry. A
482 high-level circulation induced for example by a pitched building roof will give a smaller relative
483 size of the upper vortex (Louka et al., 2000), corresponding to a higher value of α (possibly
484 equivalent to 0.9). Large eddy simulations of street canyons by Li et al. (2012) suggested that the
485 street bottom heating may have a strong impact on the flow pattern within a deep street canyon
486 (AR=2), i.e. the value of α can about 0.44 under the neutral condition, about 0.46 under weak
487 heating and about 0.9 under strong heating. There is clear evidence in Figure 12 that $C_{NO_2,L}$ is
488 significantly affected by the box height ratio. Extremely high levels of $C_{NO_2,L}$ are observed for
489 smaller box height ratios, e.g. with a maximum value of about 520 ppb for Case HB-LL with α
490 $= 0.1$. This small box height ratio represents the case that pollutants are essentially trapped in a low
491 volume part of the street canyon under poor ventilation conditions. This is similar to the secondary
492 smaller eddies near the street corner, where levels of pollutants can be extremely high. The
493 exchange velocity between lower and upper boxes (indicated by a lower value of $w_{t,L}$ in Figure 3) is
494 the lowest for Case HB-LL. It is observed that almost all of the scenarios (including trajectory
495 2005-2020) in Case HB-LL are expected to breach the UK air quality standard for hourly NO_2 , for
496 this idealised scenario, except for scenarios with extremely low emissions, shown as Figure 12a. As
497 the box height ratio increases, the solid red curve in Figure 12 shifts towards scenarios with higher
498 emissions across the trajectory for predicted emissions 2005-2020. For Case HB-H and Case HB-
499 HH, the TRES falls into the region below the UK air quality standard for hourly NO_2 . The box

500 height ratio is mainly determined by the flow structure in the street canyon. Therefore,
501 understanding the flow characteristics in a street canyon is of vital importance; numerical modelling
502 approaches can provide predictions of flow patterns at high spatial and temporal resolution within
503 street canyons. The detailed results along the selected lines for analysis, shown as Figure 4f, are
504 presented below.

505 Figure 13 shows the transects of $C_{NO_2,L}$ (ppb) for Case HB-LL, Case HB-L, Case BASE, Case HB-
506 H and Case HB-HH through the selected lines for analysis in Figure 4f. It can be seen that there is
507 an increase of $C_{NO_2,L}$ with the increase of E_{VOCs} and E_{NOx} . This increasing tendency is extremely
508 significant for Case HB-LL with the lowest box height ratio ($\alpha = 0.1$), i.e. 207 ppb difference for
509 Figure 13a, 302 ppb difference for Figure 13b and 461 ppb difference for Figure 13c. For other box
510 height ratios in Figure 13a-c, the concentration difference is around 100 ppb, much lower than that
511 for Case HB-LL. The direct contributions of NO_x emissions to $C_{NO_2,L}$ for cases with different box
512 height ratios are represented by the series of radiating lines in Figure 13b, which also indicates the
513 importance of photochemistry in converting NO to NO_2 , rather than the contribution from direct
514 emissions of NO_2 . A rapid increase of the chemically induced NO_2 for smaller E_{NOx} is also observed.
515 Figure 13d shows that there is a decrease of $C_{NO_2,L}$ with years for the corresponding predicted
516 emissions. However, the air quality is still worse for Case HB-LL and Case HB-L, i.e. about 4
517 times and 2 times of the UK air quality standard for hourly NO_2 for the year 2005, for this idealised
518 scenario.

519 Figure 14 shows the effect of the box height ratio (α) on $\phi_{NO_2,L}$ (%), i.e. the percentage of
520 overestimation for NO_2 in the lower canyon, by the ‘one-box’ model. There are significant changes
521 of $\phi_{NO_2,L}$ with the changes of the box height ratio, i.e. (-82.22 %, -57.37 %) for Case HB-LL with
522 $\alpha = 0.1$, (-54.15 %, -30.26 %) for Case HB-L with $\alpha = 0.3$, (-33.49 %, -17.07 %) for Case BASE
523 with $\alpha = 0.5$, (-17.71 %, -8.63 %) for Case HB-H with $\alpha = 0.7$ and (-5.27 %, -2.59 %) for Case HB-
524 HH with $\alpha = 0.9$. This indicates that for a higher box height ratio, the ‘one-box’ model more

525 accurately predicts NO_2 concentrations, as referenced to the coupled-two-box simulation. It is also
526 noted that $\phi_{\text{NO}_2,L}$ is less sensitive to emissions of NO_x and VOCs when the box height ratio is
527 higher. For the extremely high box height ratios, the upper box plays a similar role as the shear
528 layer, where active exchange takes place. In such a situation, the two-box model can approximate to
529 the one-box model.

530 Figure 15 illustrates the transects of $\phi_{\text{NO}_2,L}$ (ppb) for Case HB-LL, Case HB-L, Case BASE, Case
531 HB-H and Case HB-HH through the selected lines for analysis in Figure 4f. Figure 15a shows that
532 the magnitude of $\phi_{\text{NO}_2,L}$ slightly increases with the increase of E_{VOCs} , i.e. from -64.94 % to -72.29 %
533 for $\alpha=0.1$, from -33.18 % to -41.62 % for $\alpha=0.3$, from -18.14% to -24.16 % for $\alpha=0.5$, from -8.98
534 % to -12.37 % for $\alpha=0.7$ and from -2.65 % to -3.65 % for $\alpha=0.9$. This indicates that the difference
535 in $\phi_{\text{NO}_2,L}$ decreases with an increase in the box height ratio, and the one box model performs better
536 for the cases with a higher box height ratio. This finding is also indicated by Figure 15b, but the
537 magnitude of $\phi_{\text{NO}_2,L}$ slightly decreases with the increase of E_{NO_x} , especially for $E_{\text{NO}_x} / E_{\text{TRES},\text{NO}_x}$ up to
538 0.5. Figure 15c also shows that there is no significant change in $\phi_{\text{NO}_2,L}$ when changing both E_{VOCs}
539 and E_{NO_x} and that $\phi_{\text{NO}_2,L}$ is mainly influenced by the box height ratio (α). Figure 15d shows that
540 $\phi_{\text{NO}_2,L}$ does not change significantly for the predicted emissions changes over the years 2005 to
541 2020, but significant contrasts are found for the cases with different box height ratios.

542 4 Conclusions

543 The bulk levels of air pollution within a street canyon, focusing on the lower heights where
544 pedestrian / human exposure takes place, are investigated using a coupled-two-box model approach,
545 which enables a wide range of emission scenarios to be considered in a computationally efficient
546 manner, whilst providing greater realism than a single, well-mixed box approach. The performance
547 of the one-box model approach (assuming the whole street canyon as a well-mixed box) was also
548 examined compared with the bulk concentrations in the lower canyon of the two-box model. Core

important parameters (i.e. heterogeneity coefficient, exchange velocity and box height ratio) related to the two-box model approach were investigated. The two-box model results identify the emission regimes and the meteorological conditions under which NO_2 in the lower canyon (street level) is in breach of air quality standards. Higher NO_2 levels were observed for the cases with higher heterogeneity coefficients (the two boxes are more segregated), or with lower exchange velocities (worse ventilation conditions) or with smaller box height ratios (reduced dilution possibly due to secondary smaller eddies in the lower canyon). The one-box model was found to systematically underestimate NO_2 levels compared with those in the lower box of the two-box model for all the test scenarios. This underestimation generally tends to worsen for higher heterogeneity coefficients, lower exchange velocities, or smaller box height ratios. This study highlights the limitation of the assumption of homogeneity in single box models for street canyon simulation, and the inherent uncertainties that must be borne in mind to appropriately interpret such model output (in particular, that a single-box treatment will systematically underestimate NO_2 as experienced at street level). The assumption of ‘exchange velocity’ adopted in the two-box model approach only represents the overall integrated effect of the dynamical flow between simplified street canyon boxes, failing to capture the structure of flow and pollutant distribution inside street canyons. The box model approach only provides mean concentrations within the boxes and assumes an instant and complete mixing, thus artificially augmenting chemical reaction rates within the boxes (i.e. generally enhancing the NO to NO_2 conversion rate such that NO_2 would be overestimated) (Zhong et al. (2015); Bright et al. (2013)). In addition, the two-box model approach (vertically segregated) is restricted to represent two vortices within a street canyon. For even taller canyons, more vortices may be formed. Future studies should adopt more photochemical boxes and use finite exchange velocities to allow an incomplete mixing across boxes (thus to be closer to the real conditions), and extend the range of scenarios to encompass the range encountered in reality. Reactive pollutant abundance could be obtained by running the two-box model if a set of parameters are provided for real urban areas as the model inputs (e.g. heterogeneity coefficient, exchange velocity, box height

ratio and emissions) although these three parameters are might be uncontrollable and site- and flow-dependent. For an application in future, it is needed to map the ‘controllable pre-defined building geometry parameters’ and meteorological conditions to the three box-model parameters we proposed in this study using available knowledge, datasets (e.g. wind tunnel experiments), and/or modelling tools (e.g. CFD). In addition, a standard procedure for setting the parameters used in the two-box model should be developed. A multi-box air quality model for a street canyon network may then be developed for practical applications.

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597 **Appendix A: RCS mechanism**
598

599 **Table A1** All reactions and rate constants included in the RCS mechanism (adopted from Bright (2013)).
600 The units of rate constants are s⁻¹ for first order reactions and ppb s⁻¹ for second order reactions. The pressure
601 is set to 10132.5 Pa and the temperature is set to 293 K.

Reactants		Products		Rate constant
1	O ₃	→ OH + OH		3.40E-6
2	NO + O ₃	→ NO ₂		4.01E-4
3	NO + NO	→ NO ₂ + NO ₂		2.63E-9
4	NO + NO ₃	→ NO ₂ + NO ₂		6.56E-1
5	OH + O ₃	→ HO ₂		1.72E-3
6	OH + H ₂	→ HO ₂		1.49E-4
7	OH + CO	→ HO ₂		5.06E-3
8	H ₂ O ₂ + OH	→ HO ₂		4.21E-2
9	HO ₂ + O ₃	→ OH		4.86E-5
10	OH + HO ₂	→		2.82E+0
11	HO ₂ + HO ₂	→ H ₂ O ₂		8.74E-2
12	HO ₂ + HO ₂	→ H ₂ O ₂		6.92E-2
13	OH + NO	→ HONO		2.54E-1
14	OH + NO ₂	→ HNO ₃		3.08E-1
15	OH + NO ₃	→ HO ₂ + NO ₂		5.01E-1
16	HO ₂ + NO	→ OH + NO ₂		2.27E-1
17	HO ₂ + NO ₂	→ HO ₂ NO ₂		3.59E-2
18	HO ₂ NO ₂	→ HO ₂ + NO ₂		3.74E-2
19	HO ₂ NO ₂ + OH	→ NO ₂		1.20E-1
20	HONO + OH	→ NO ₂		2.58E-2
21	HNO ₃ + OH	→ NO ₃		4.08E-3
22	H ₂ O ₂	→ OH + OH		7.11E-6
23	NO ₂	→ NO + O ₃		9.20E-3
24	NO ₃	→ NO		2.34E-2
25	NO ₃	→ NO ₂ + O ₃		1.83E-1
26	HONO	→ OH + NO		2.02E-3

27	HNO ₃			→	OH	+	NO ₂			6.30E-7
28	CH ₄	+	OH	→	CH ₃ O ₂					1.39E-4
29	C ₂ H ₄	+	OH	→	HOCH ₂ CH ₂ O ₂					2.00E-1
30	C ₃ H ₆	+	OH	→	RN ₉ O ₂					7.19E-1
31	C ₂ H ₄	+	O ₃	→	HCHO	+	CO	+	HO ₂ + OH	4.46E-9
32	C ₂ H ₄	+	O ₃	→	HCHO	+	HCOOH			2.99E-8
33	C ₃ H ₆	+	O ₃	→	HCHO	+	CH ₃ O ₂	+	CO + OH	8.18E-8
34	C ₃ H ₆	+	O ₃	→	HCHO	+	CH ₃ CO ₂ H			1.45E-7
35	C ₅ H ₈	+	OH	→	RU14O2					2.58E+0
36	C ₅ H ₈	+	O ₃	→	UCARB10	+	CO	+	HO ₂ + OH	7.76E-8
37	C ₅ H ₈	+	O ₃	→	UCARB10	+	HCOOH			2.10E-7
38	HCHO			→	CO	+	HO ₂	+	HO ₂	3.05E-5
39	HCHO			→	H ₂	+	CO			4.61E-5
40	CH ₃ CHO			→	CH ₃ O ₂	+	HO ₂	+	CO	5.07E-6
41	HCHO	+	OH	→	HO ₂	+	CO			2.35E-1
42	CH ₃ CHO	+	OH	→	CH ₃ CO ₃					4.02E-1
43	CH ₃ OH	+	OH	→	HO ₂	+	HCHO			2.31E-2
44	C ₂ H ₅ OH	+	OH	→	CH ₃ CHO	+	HO ₂			7.24E-2
45	C ₂ H ₅ OH	+	OH	→	HOCH ₂ CH ₂ O ₂					9.23E-3
46	HCOOH	+	OH	→	HO ₂					1.13E-2
47	CH ₃ CO ₂ H	+	OH	→	CH ₃ O ₂					2.00E-2
48	CH ₃ O ₂	+	NO	→	HCHO	+	HO ₂	+	NO ₂	1.95E-1
49	HOCH ₂ CH ₂ O ₂	+	NO	→	HCHO	+	HCHO	+	HO ₂ + NO ₂	1.68E-1
50	HOCH ₂ CH ₂ O ₂	+	NO	→	HOCH ₂ CHO	+	HO ₂	+	NO ₂	4.84E-2
51	RN ₉ O ₂	+	NO	→	CH ₃ CHO	+	HCHO	+	HO ₂ + NO ₂	2.13E-1
52	CH ₃ CO ₃	+	NO	→	CH ₃ O ₂	+	NO ₂			5.10E-1
53	HOCH ₂ CO ₃	+	NO	→	HO ₂	+	HCHO	+	NO ₂	5.10E-1
54	RU14O ₂	+	NO	→	UCARB12	+	HO ₂	+	NO ₂	4.93E-2
55	RU14O ₂	+	NO	→	UCARB10	+	HCHO	+	HO ₂ + NO ₂	1.46E-1
56	RU12O ₂	+	NO	→	CH3CO3	+	HOCH ₂ CHO	+	NO ₂	1.52E-1
57	RU12O ₂	+	NO	→	CARB7	+	CO	+	HO ₂ + NO ₂	6.52E-2
58	RU10O ₂	+	NO	→	CH3CO3	+	HOCH ₂ CHO	+	NO ₂	1.09E-1

59	RU10O ₂	+	NO	→	CARB6	+	HCHO	+	HO ₂	+	NO ₂	6.52E-2
60	RU10O ₂	+	NO	→	CARB7	+	HCHO	+	HO ₂	+	NO ₂	4.35E-2
61	CH ₃ O ₂	+	NO	→	CH ₃ NO ₃							1.95E-4
62	HOCH ₂ CH ₂ O ₂	+	NO	→	HOC ₂ H ₄ NO ₃							1.09E-3
63	RN ₉ O ₂	+	NO	→	RN9NO ₃							4.56E-3
64	RU14O ₂	+	NO	→	RU14NO ₃							2.17E-2
65	CH ₃ O ₂	+	HO ₂	→	CH ₃ OOH							1.52E-1
66	HOCH ₂ CH ₂ O ₂	+	HO ₂	→	HOC ₂ H ₄ OOH							3.62E-1
67	RN9O ₂	+	HO ₂	→	RN9OOH							3.20E-1
68	CH ₃ CO ₃	+	HO ₂	→	CH ₃ CO ₃ H							3.75E-1
69	HOCH ₂ CO ₃	+	HO ₂	→	HOCH ₂ CO ₃ H							3.75E-1
70	RU14O ₂	+	HO ₂	→	RU14OOH							4.74E-1
71	RU12O ₂	+	HO ₂	→	RU12OOH							4.35E-1
72	RU10O ₂	+	HO ₂	→	RU10OOH							3.85E-1
73	CH ₃ O ₂			→	HCHO	+	HO ₂					6.22E-3*
74	CH ₃ O ₂			→	HCHO							6.32E-3*
75	CH ₃ O ₂			→	CH ₃ OH							6.32E-3*
76	HOCH ₂ CH ₂ O ₂			→	HOCH ₂ CHO	+	HO ₂					1.12E-2*
77	RN9O ₂			→	CH ₃ CHO	+	HCHO	+	HO ₂			2.20E-2*
78	CH ₃ CO ₃			→	CH ₃ O ₂							2.50E-1*
79	HOCH ₂ CO ₃			→	HCHO	+	HO ₂					2.50E-1*
80	RU14O ₂			→	UCARB12	+	HO ₂					1.08E-2*
81	RU14O ₂			→	UCARB10	+	HCHO	+	HO ₂			3.20E-2*
82	RU12O ₂			→	CH ₃ CO ₃	+	HOCH ₂ CHO					3.51E-2*
83	RU12O ₂			→	CARB7	+	HOCH ₂ CHO	+	HO ₂			1.50E-2*
84	RU10O ₂			→	CH ₃ CO ₃	+	HOCH ₂ CHO					2.50E-2*
85	RU10O ₂			→	CARB6	+	HCHO	+	HO ₂			1.50E-2*
86	RU10O ₂			→	CARB7	+	HCHO	+	HO ₂			1.00E-2*
87	CARB7			→	CH ₃ CO ₃	+	HCHO	+	HO ₂			3.36E-6
88	HOCH ₂ CHO			→	HCHO	+	CO	+	HO ₂	+	HO ₂	1.77E-5
89	UCARB10			→	CH ₃ CO ₃	+	HCHO	+	HO ₂			1.62E-5
90	CARB6			→	CH ₃ CO ₃	+	CO	+	HO ₂			1.26E-4

91	UCARB12			→	CH ₃ CO ₃	+	HOCH2CHO	+	CO	+	HO2	1.62E-5
92	CARB7	+	OH	→	CARB6	+	HO ₂					7.51E-2
93	UCARB10	+	OH	→	RU10O ₂							6.26E-1
94	UCARB10	+	O ₃	→	HCHO	+	CH ₃ CO ₃	+	CO	+	OH	4.21E-8
95	UCARB10	+	O ₃	→	HCHO	+	CARB6	+	H ₂ O ₂			2.93E-8
96	HOCH ₂ CHO	+	OH	→	HOCH ₂ CO ₃							2.50E-1
97	CARB6	+	OH	→	CH ₃ CO ₃	+	CO					4.31E-1
98	UCARB12	+	OH	→	RU12O ₂							1.13E-0
99	UCARB12	+	O ₃	→	HOCH ₂ CHO	+	CH ₃ CO ₃	+	CO	+	OH	5.35E-7
100	UCARB12	+	O ₃	→	HOCH ₂ CHO	+	CARB6	+	H ₂ O ₂			6.61E-8
101	CH ₃ NO ₃			→	HCHO	+	HO ₂	+	NO ₂			8.96E-7
102	CH ₃ NO ₃	+	OH	→	HCHO	+	NO ₂					9.33E-3
103	HOC ₂ H ₄ NO ₃	+	OH	→	HOCH ₂ CHO	+	NO ₂					2.73E-2
104	RN9NO ₃	+	OH	→	CARB7	+	NO ₂					3.28E-2
105	RU14NO ₃	+	OH	→	UCARB12	+	NO ₂					1.39E+0
106	CH ₃ OOH			→	HCHO	+	HO ₂	+	OH			5.44E-6
107	CH ₃ CO ₃ H			→	CH ₃ O ₂	+	OH					5.44E-6
108	HOCH ₂ CO ₃ H			→	HCHO	+	HO ₂	+	OH			5.44E-6
109	RU14OOH			→	UCARB12	+	HO ₂	+	OH			1.37E-6
110	RU14OOH			→	UCARB10	+	HCHO	+	HO ₂	+	OH	4.07E-6
111	RU12OOH			→	CARB6	+	HOCH2CHO	+	HO ₂	+	OH	5.44E-6
112	RU10OOH			→	CH ₃ CO ₃	+	HOCH2CHO	+	OH			5.44E-6
113	HOC ₂ H ₄ OOH			→	HCHO	+	HCHO	+	HO ₂	+	OH	5.44E-6
114	RN9OOH			→	CH ₃ CHO	+	HCHO	+	HO ₂	+	OH	5.44E-6
115	CH ₃ OOH	+	OH	→	CH ₃ O ₂							9.10E-1
116	CH ₃ OOH	+	OH	→	HCHO	+	OH					4.79E-1
117	CH ₃ CO ₃ H	+	OH	→	CH ₃ CO ₃							9.27E-2
118	HOCH ₂ CO ₃ H	+	OH	→	HOCH ₂ CO ₃							1.55E-1
119	RU14OOH	+	OH	→	UCARB12	+	OH					1.88E+0
120	RU12OOH	+	OH	→	RU12O ₂							7.51E-1
121	RU10OOH	+	OH	→	RU10O ₂							7.51E-1
122	HOC ₂ H ₄ OOH	+	OH	→	HOCH ₂ CHO	+	OH					5.34E-1

123	RN9OOH	+	OH	→	CARB7	+	OH		6.26E-1
124	CH ₃ CO ₃	+	NO ₂	→	PAN				2.68E-1
125	PAN			→	CH ₃ CO ₃	+	NO ₂		1.51E-4
126	HOCH ₂ CO ₃	+	NO ₂	→	PHAN				2.68E-1
127	PHAN			→	HOCH ₂ CO ₃	+	NO ₂		1.51E-4
128	PAN	+	OH	→	HCHO	+	CO	+	NO ₂
129	PHAN	+	OH	→	HCHO	+	CO	+	NO ₂
130	RU12O ₂	+	NO ₂	→	RU12PAN				1.63E-2
131	RU12PAN			→	RU12O ₂	+	NO ₂		1.51E-4
132	RU10O ₂	+	NO ₂	→	MPAN				1.10E-2
133	MPAN			→	RU10O ₂	+	NO ₂		1.51E-4
134	MPAN	+	OH	→	CARB7	+	CO	+	NO ₂
135	RU12PAN	+	OH	→	UCARB10	+	NO ₂		6.31E-1
136	NO ₂	+	O ₃	→	NO ₃				7.65E-7

Note: * means peroxy radical summation, which is applied to the RO₂ permutation reactions.

[RO₂] = [CH₃O₂] + [HOCH₂CH₂O₂] + [RN9O₂] + [CH₃CO₃] + [HOCH₂CO₃] + [RU14O₂] + [RU12O₂] + [RU10O₂]

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612 **Table 1 Overview of the model scenarios**

Case	Heterogeneity coefficient (η)	Exchange velocity $w_{t,0}$ (m s^{-1})	Box height ratio (α)
BASE	0.5	0.02	0.5
HC-LL	0.1	0.02	0.5
HC-L	0.3	0.02	0.5
HC-H	0.7	0.02	0.5
HC-HH	0.9	0.02	0.5
EX-LL	0.5	0.012	0.5
EX-L	0.5	0.016	0.5
EX-H	0.5	0.024	0.5
EX-HH	0.5	0.028	0.5
BH-LL	0.5	0.02	0.1
BH-L	0.5	0.02	0.3
BH-H	0.5	0.02	0.7
BH-H	0.5	0.02	0.9
Note: ‘BASE’ is the base case. ‘HC’ denotes the heterogeneity coefficient; ‘EX’ denotes the exchange velocity; ‘BH’ denotes the box height ratio. ‘LL’, ‘L’, ‘H’ and ‘HH’ represent a even lower, lower, higher and even higher value than the corresponding component in the case BASE, respectively.			

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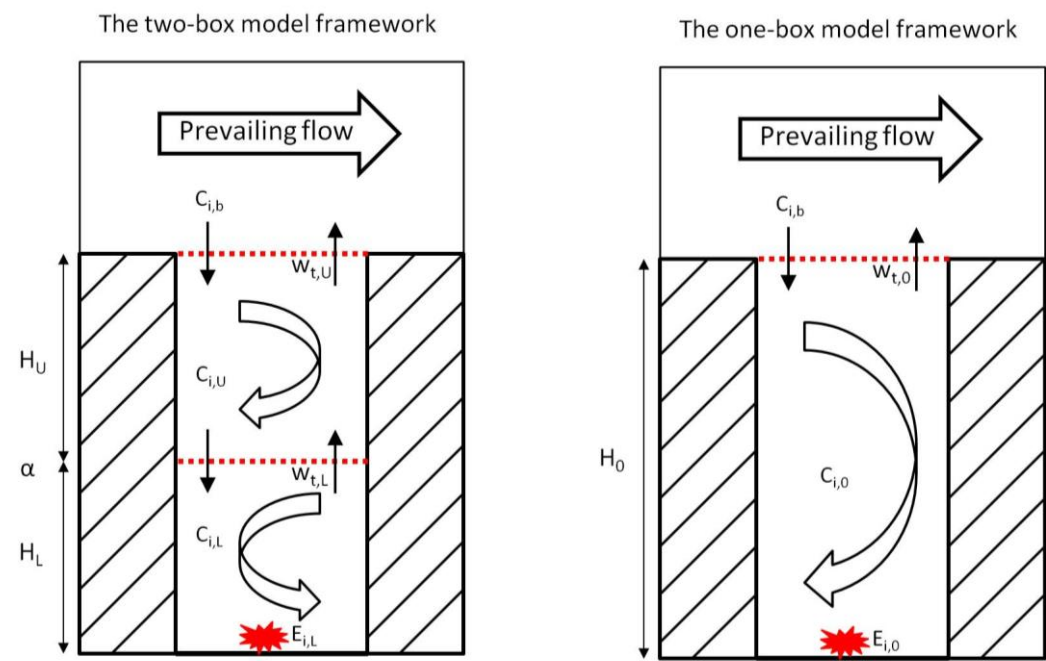
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(a)

(b)



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624 **Figure 1 Framework of the coupled two-box and one-box models (see text for details).**

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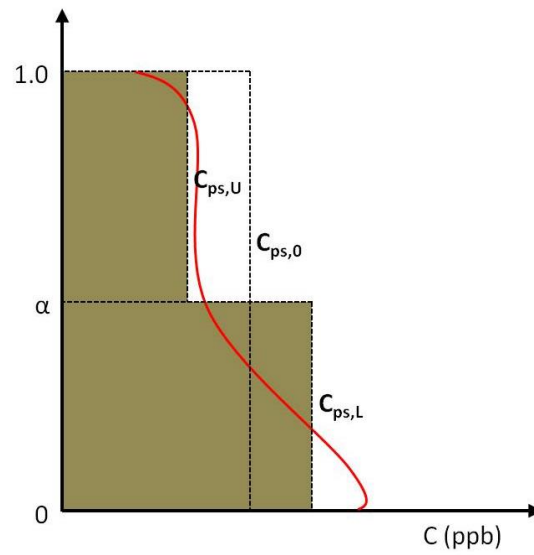
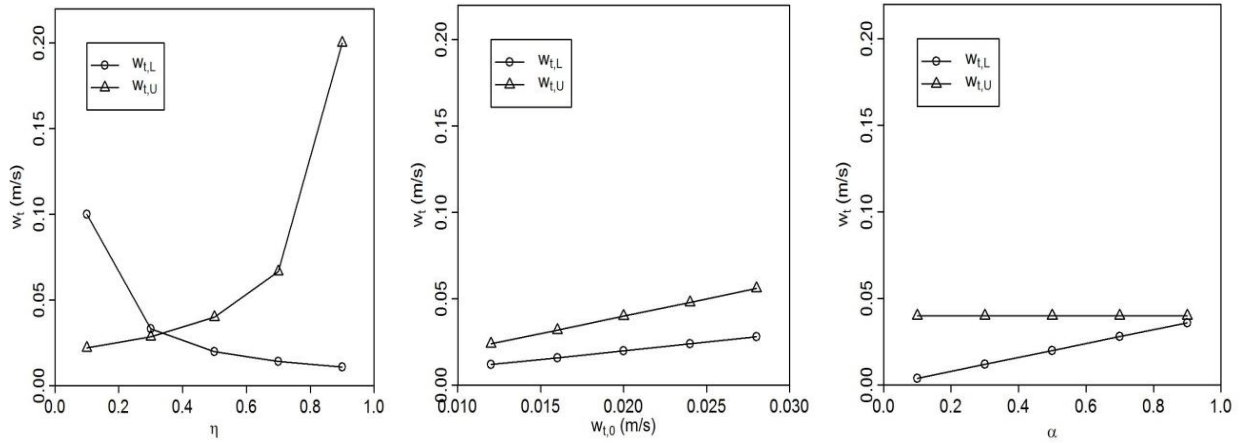


Figure 2 Schematic diagram of the vertical concentration profile and bulk concentrations in the lower and upper boxes, and in the whole street canyon of passive scalar.

650 (a) (b) (c)

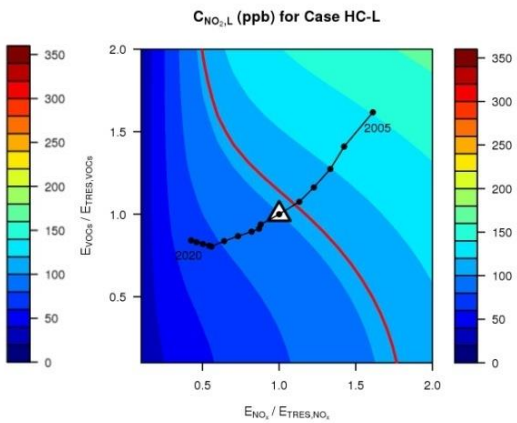
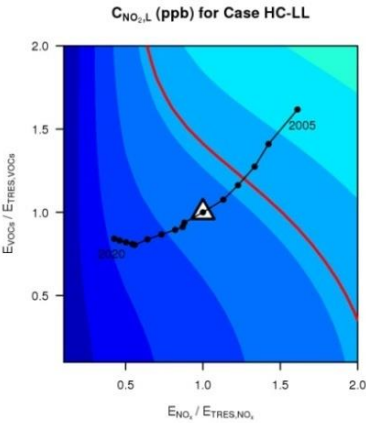


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652 **Figure 3** The relationship between exchange velocities for the two-box model against (a) η when $\alpha = 0.5$, (b)
653 $w_{t,0}$ when $\alpha = 0.5$ and $\eta = 0.5$, and (c) α when $\eta = 0.5$ and $w_{t,0} = 0.02$ (m s⁻¹). See Equations 13-14.

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(a)

(b)

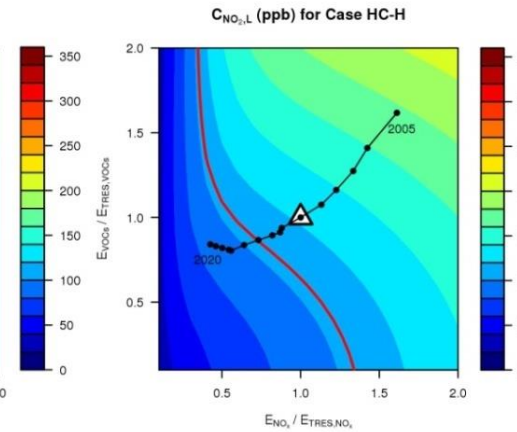
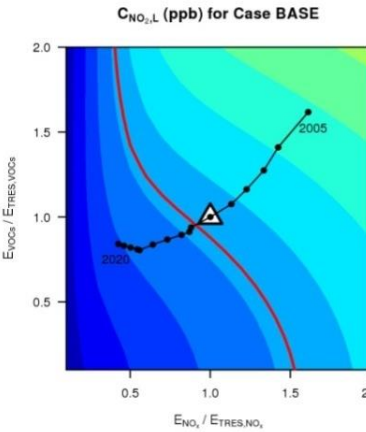


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(c)

(d)

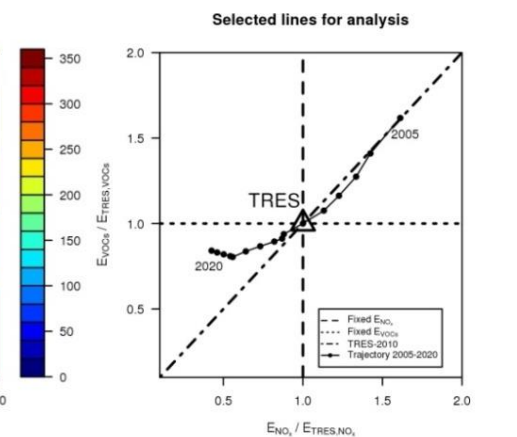
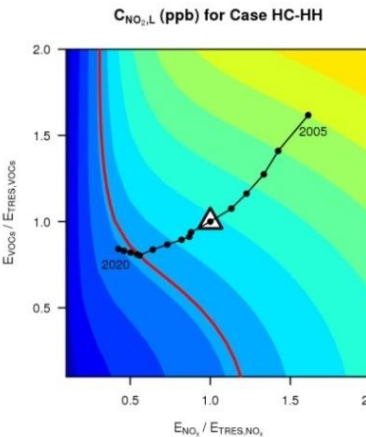


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(e)

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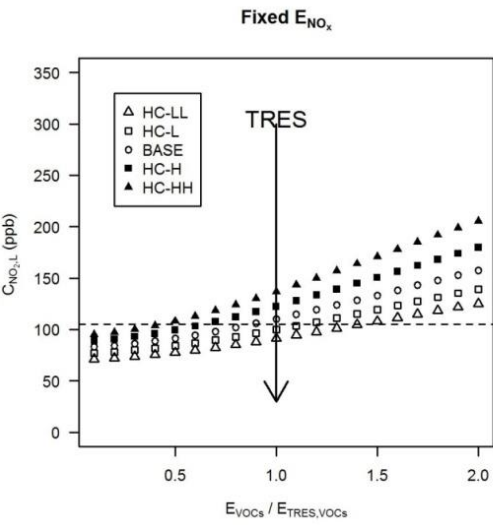
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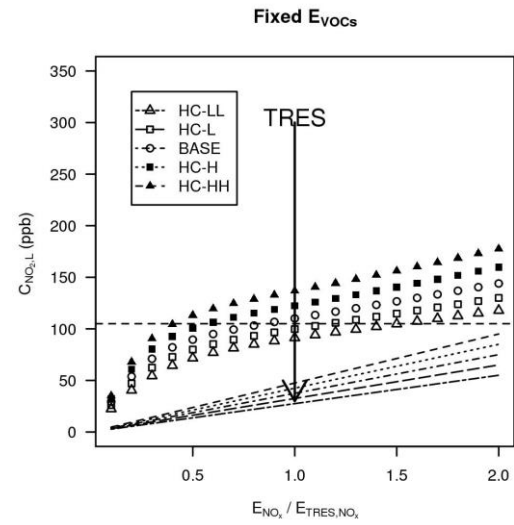
Figure 4 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, in the (a) Case HC-LL ($\eta=0.1$), (b) Case HC-L ($\eta=0.3$), (c) Case BASE ($\eta=0.5$), (d) Case HC-H ($\eta=0.7$), (e) Case HC-HH ($\eta=0.9$) and (f) Selected lines for analysis. E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed. The solid red curves denote the UK air quality standard for hourly NO_2 (105 ppb).

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(a)



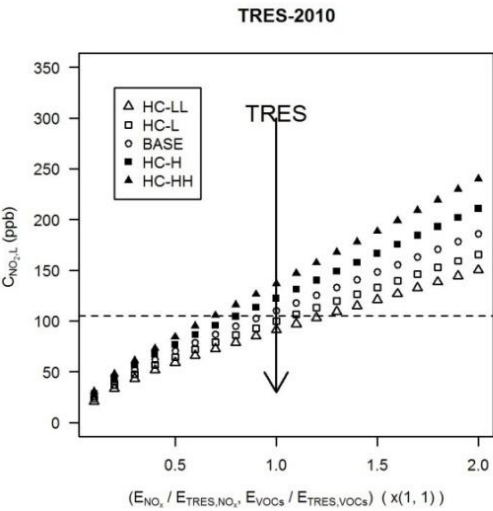
(b)



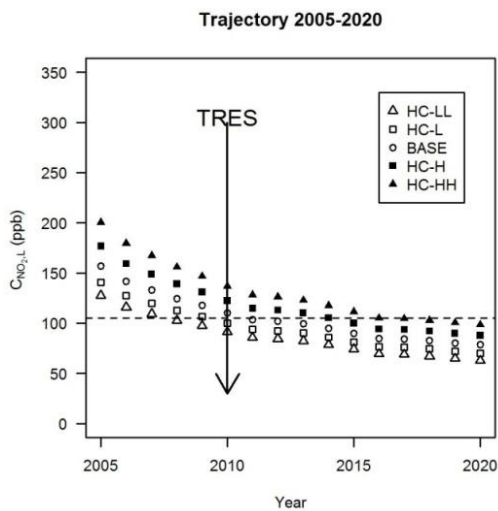
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(c)



(d)



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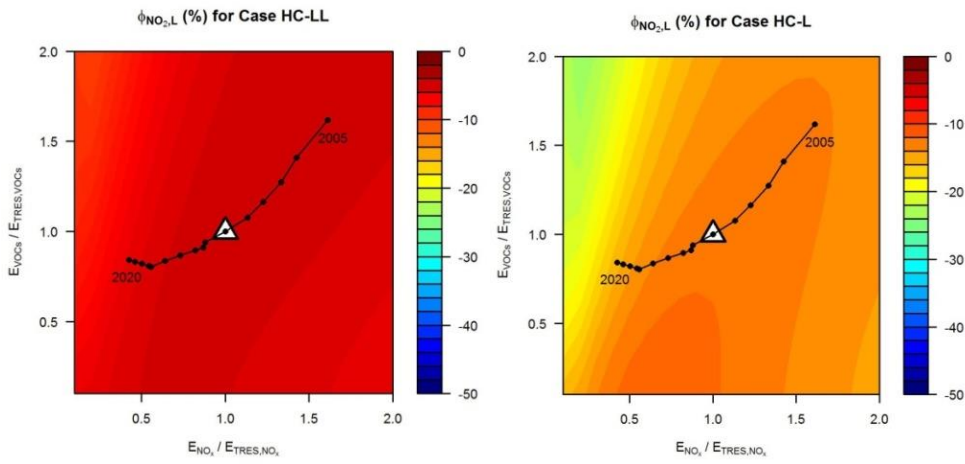
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Figure 5 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, for (a) “Fixed E_{NO_x} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES (The direct contributions of NO_x emissions to $C_{NO_2,L}$ are indicated by a series of radiating lines, running from highest to lowest for the cases from HC-HH to HC-LL.), (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying η . E_{VOCs} and E_{NO_x} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. The dashed line indicates the UK air quality standard for hourly NO_2 (105 ppb).

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(a)

(b)

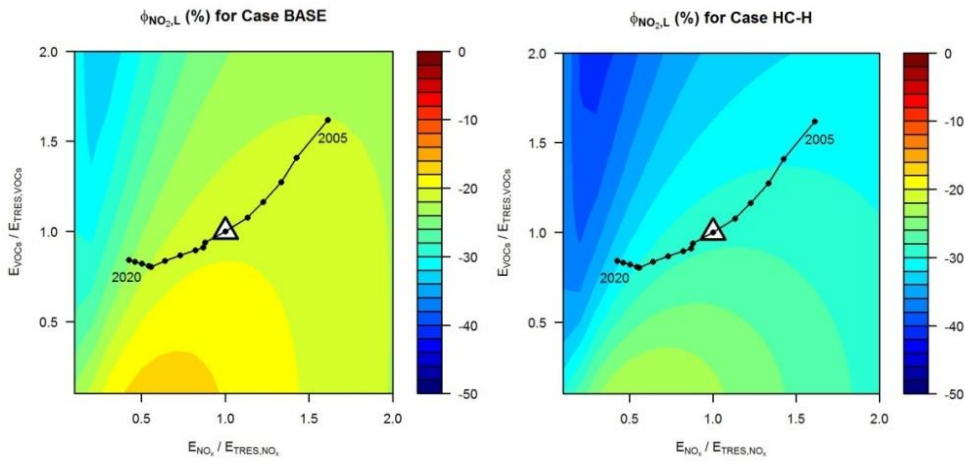


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(c)

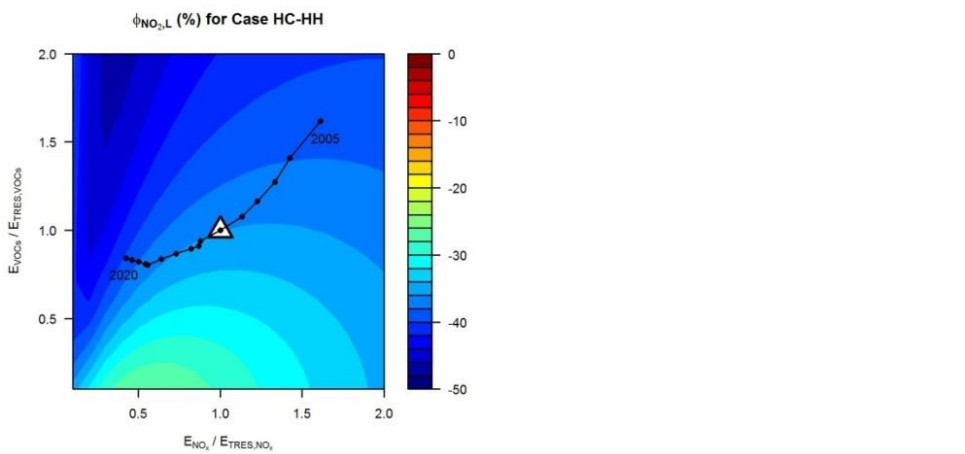
(d)



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(e)



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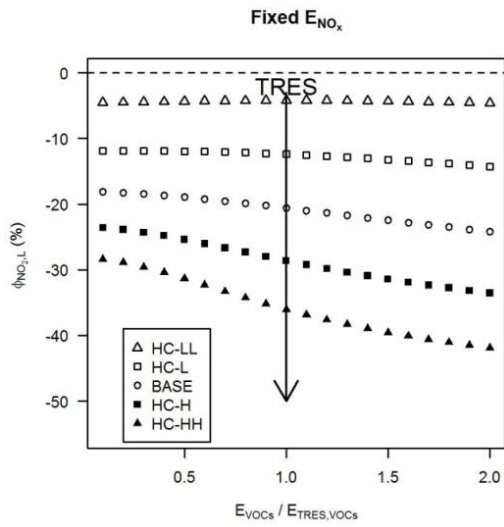
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Figure 6 $\phi_{NO_2,L}$ (%), i.e. the percentage of overestimation for NO_2 in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, in the (a) Case HC-LL ($\eta=0.1$), (b) Case HC-L ($\eta=0.3$), (c) Case BASE ($\eta=0.5$), (d) Case HC-H ($\eta=0.7$), (e) Case HC-HH ($\eta=0.9$). E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed.

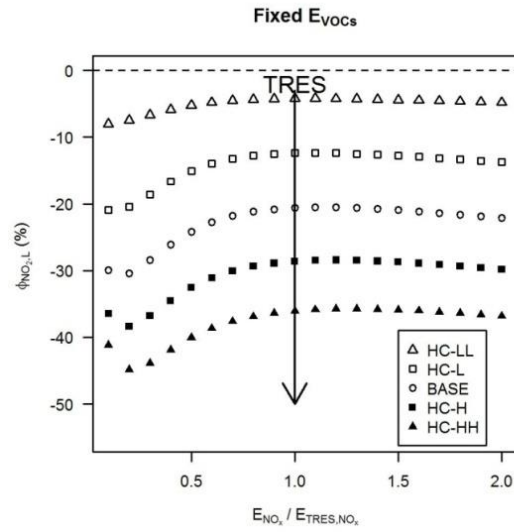
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(a)



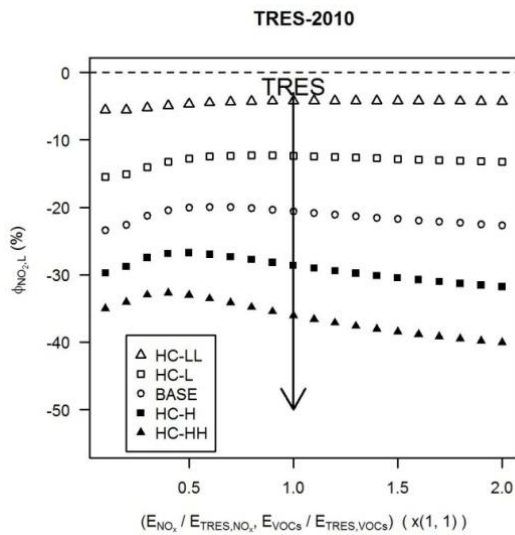
(b)



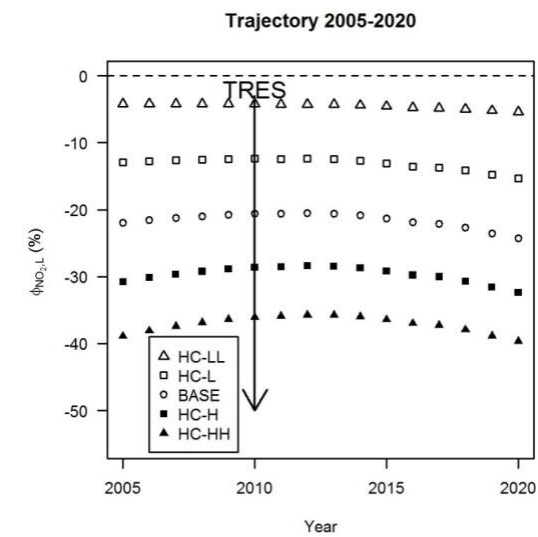
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(c)



(d)



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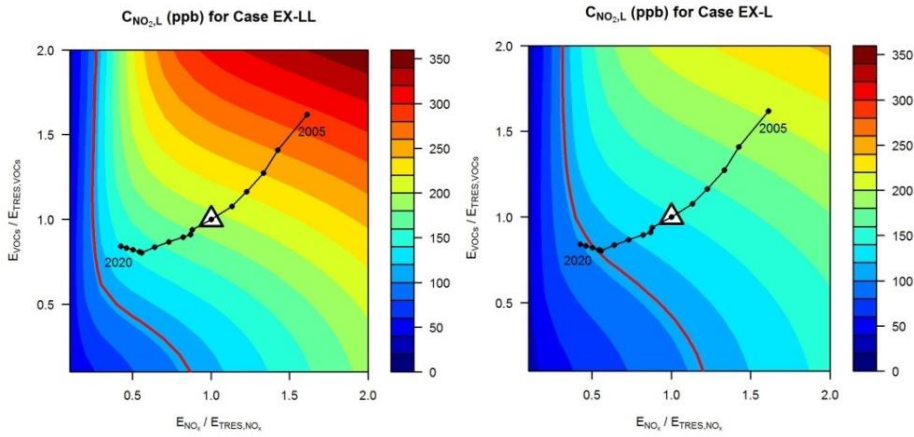
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Figure 7 $\phi_{NO_2,L}$ (%), i.e. the percentage of overestimation for NO_2 in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, for (a) “Fixed E_{NOx} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES, (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying η . E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010.

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(a)

(b)

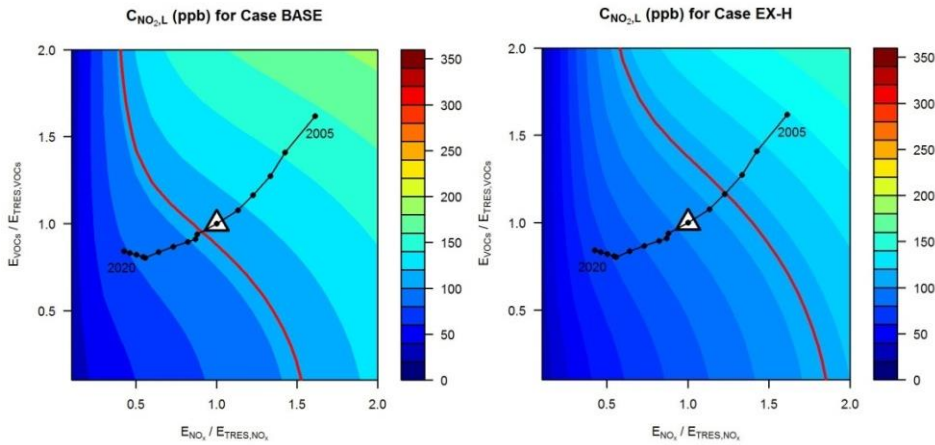


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(c)

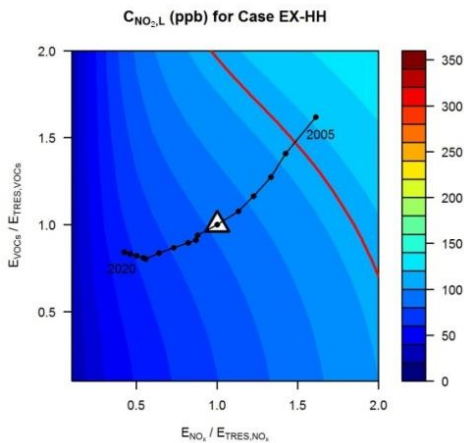
(d)



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(e)



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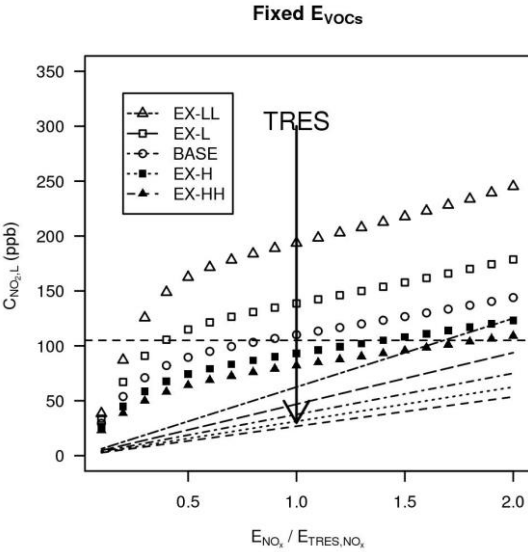
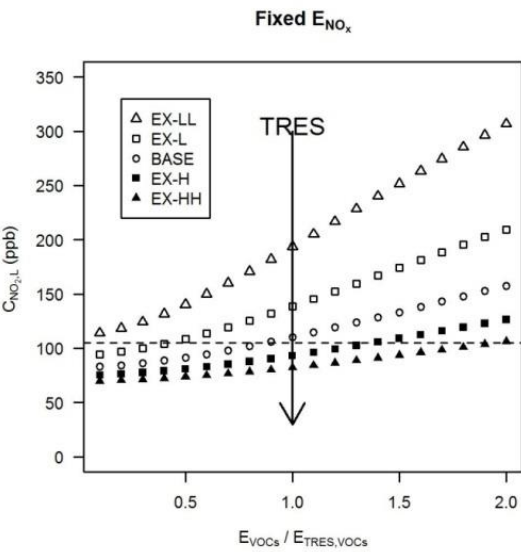
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Figure 8 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, in the (a) Case EX-LL ($w_{t,0} = 0.012 \text{ m s}^{-1}$), (b) Case EX-L ($w_{t,0} = 0.016 \text{ m s}^{-1}$), (c) Case BASE ($w_{t,0} = 0.02 \text{ m s}^{-1}$), (d) Case EX-H ($w_{t,0} = 0.024 \text{ m s}^{-1}$) and (e) Case EX-HH ($w_{t,0} = 0.028 \text{ m s}^{-1}$). E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by \triangle), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed. The solid red curves denote the UK air quality standard for hourly NO_2 (105 ppb).

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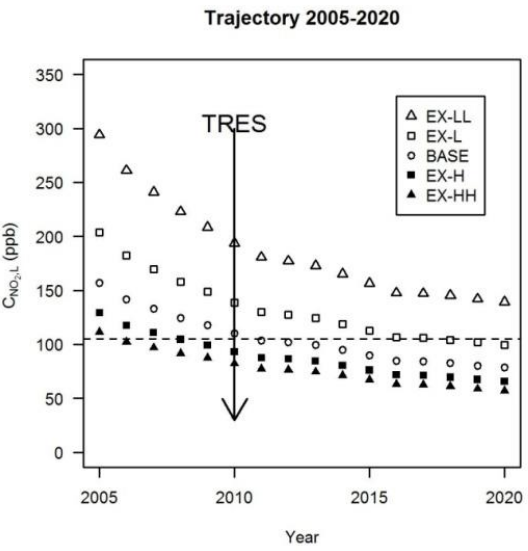
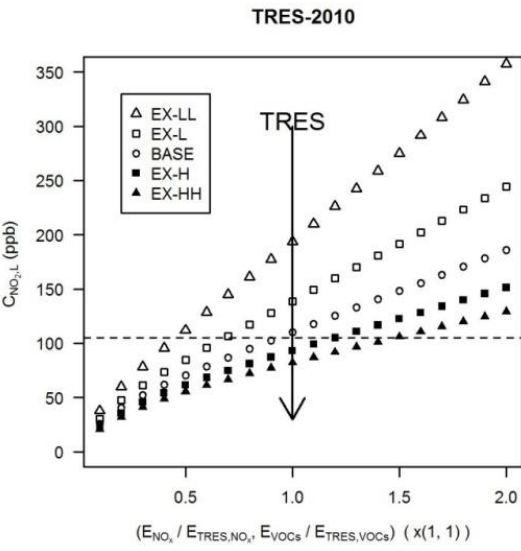
(a) (b)



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(c) (d)



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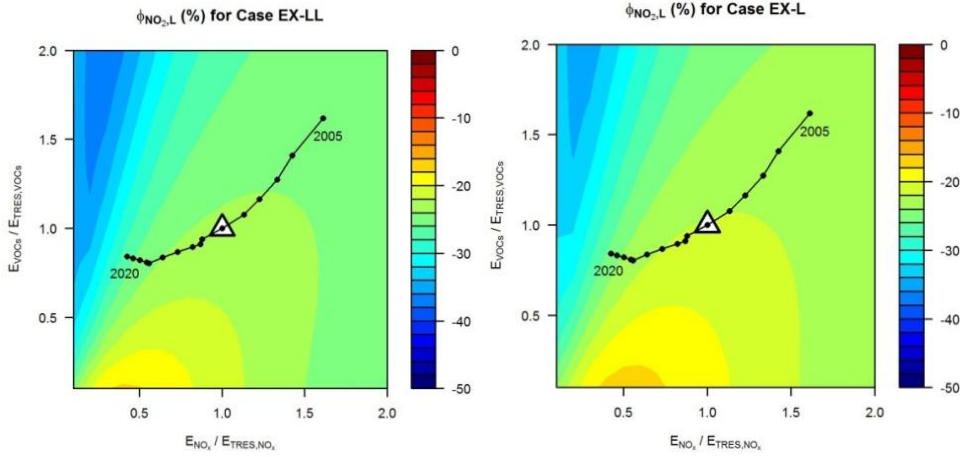
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Figure 9 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, for (a) “Fixed E_{NOx} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES (The direct contributions of NO_x emissions to $C_{NO_2,L}$ are indicated by a series of radiating lines, running from highest to lowest for the cases from EX-LL to HC-HH.), (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying $w_{t,0} \cdot E_{VOCs}$ and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. The dashed line indicates the UK air quality standard for hourly NO_2 (105 ppb).

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(a)

(b)

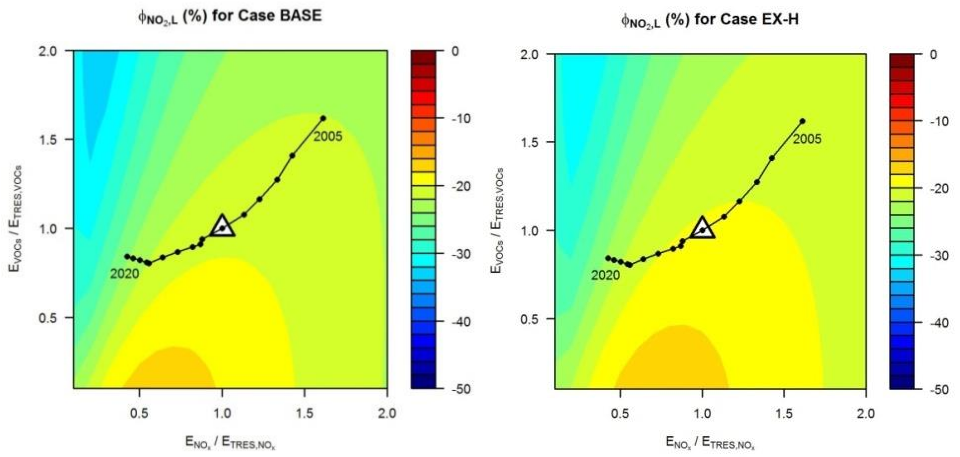


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(c)

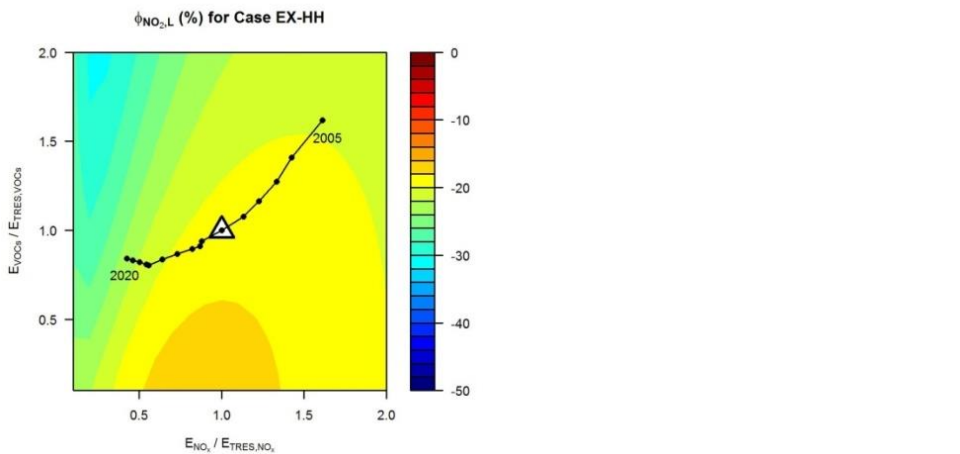
(d)



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(e)



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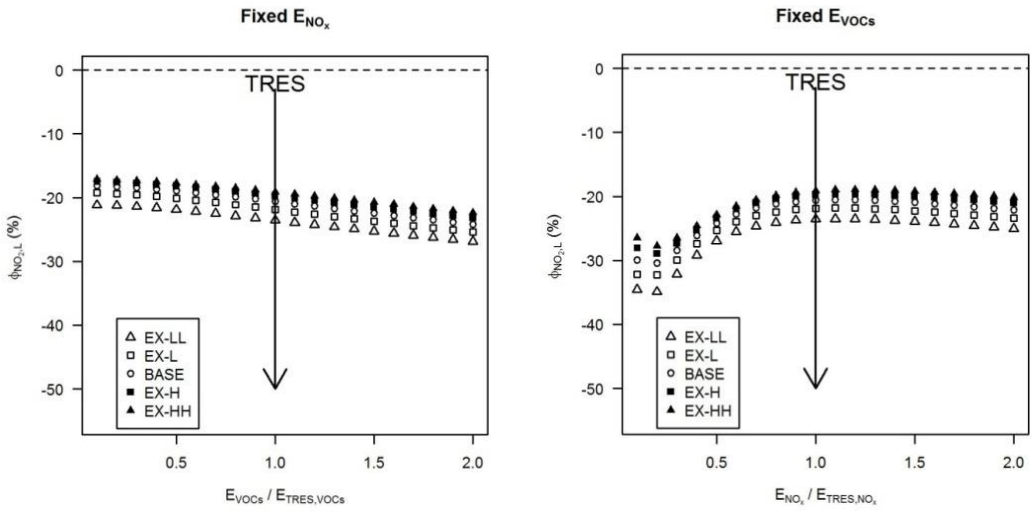
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Figure 10 $\phi_{NO_2,L}$ (%), i.e. the percentage of overestimation for NO_2 in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, in the (a) Case EX-LL ($w_{t,0} = 0.012 \text{ m s}^{-1}$), (b) Case EX-L ($w_{t,0} = 0.016 \text{ m s}^{-1}$), (c) Case BASE ($w_{t,0} = 0.02 \text{ m s}^{-1}$), (d) Case EX-H ($w_{t,0} = 0.024 \text{ m s}^{-1}$) and (e) Case EX-HH ($w_{t,0} = 0.028 \text{ m s}^{-1}$). E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed.

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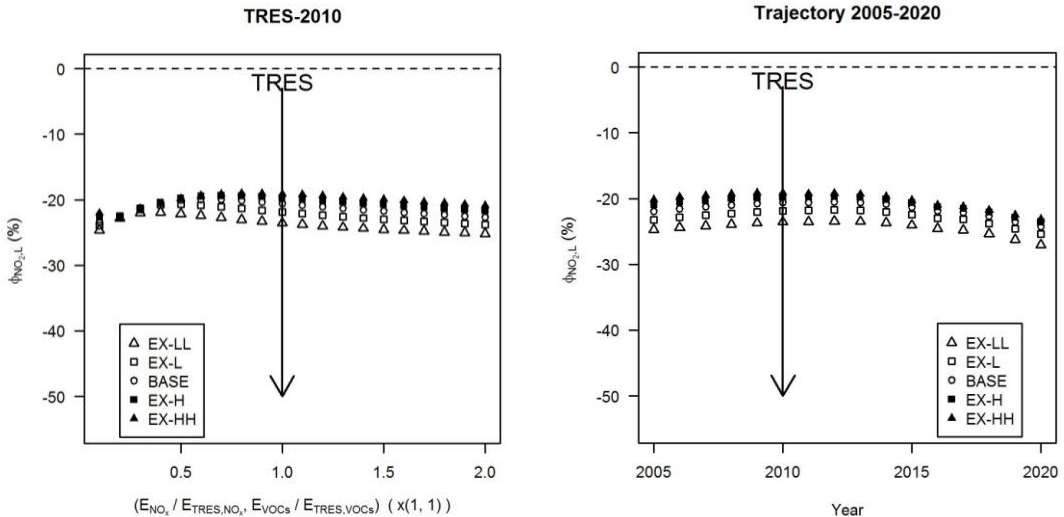
(a) (b)



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(c) (d)



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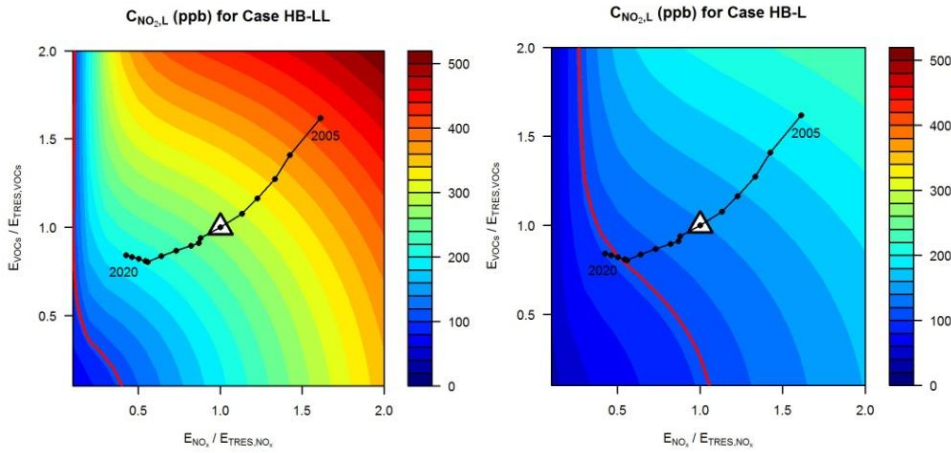
Figure 11 $\phi_{NO_2,L}$ (%), i.e. the percentage of overestimation for NO_2 in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, for (a) “Fixed E_{NOx} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES, (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying $w_{t,0}$. E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010.

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(a)

(b)

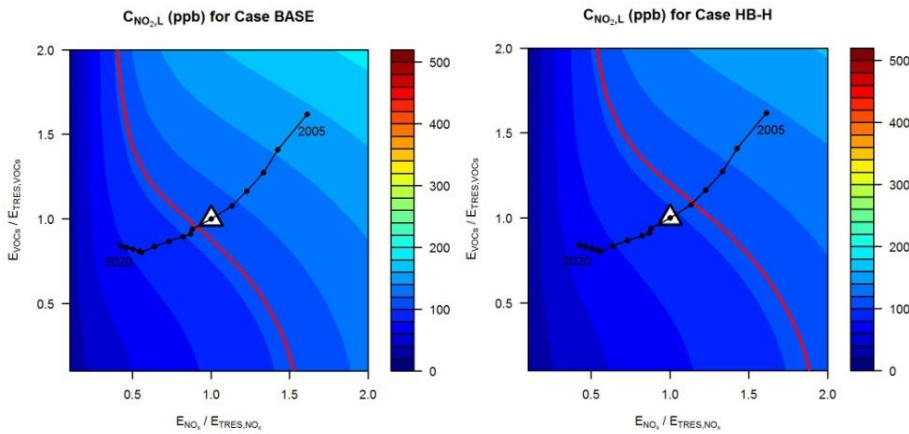


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(c)

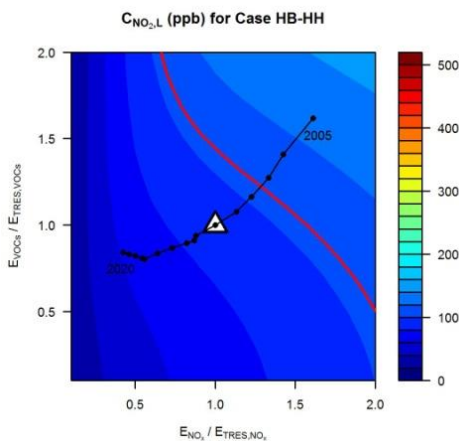
(d)



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(e)



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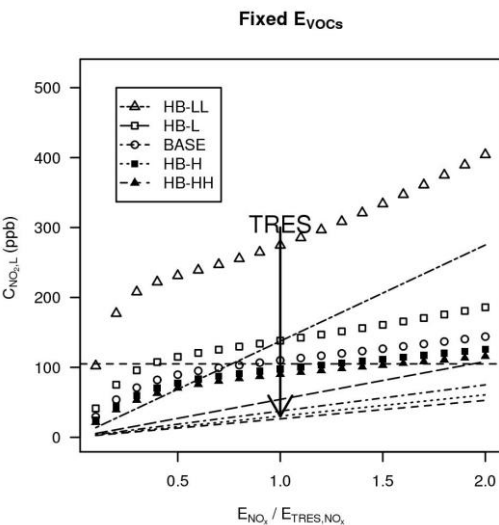
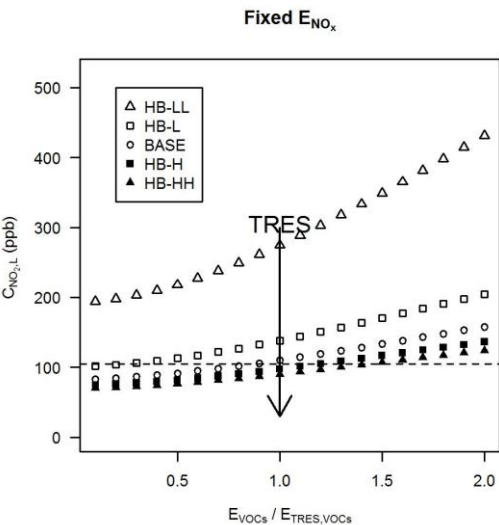
Figure 12 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, in the (a) Case HB-LL ($\alpha = 0.1$), (b) Case HB-L ($\alpha = 0.3$), (c) Case BASE ($\alpha = 0.5$), (d) Case HB-H ($\alpha = 0.7$), and (e) Case HB-HH ($\alpha = 0.9$). E_{VOCs} and E_{NO_x} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed. The solid red curves denote the UK air quality standard for hourly NO_2 (105 ppb).

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(a)

(b)

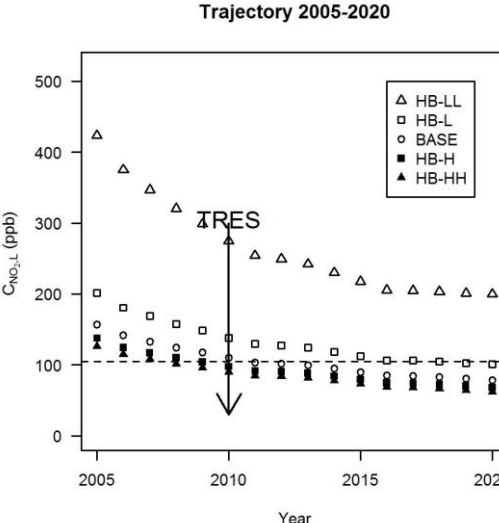
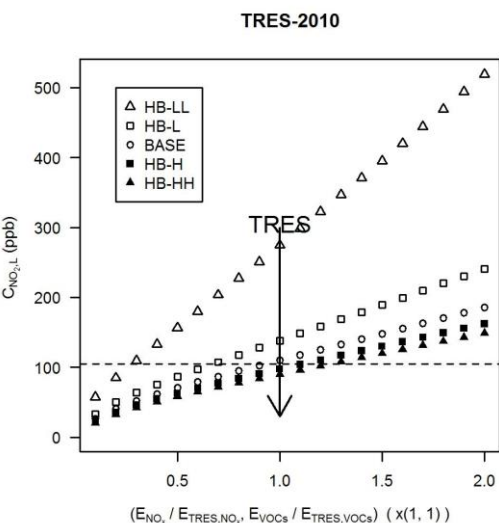


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(c)

(d)



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Figure 13 $C_{NO_2,L}$ (ppb), i.e. the concentration in the lower box derived from the “two-box” model, for (a) “Fixed E_{NO_x} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES (The direct contributions of NO_x emissions to $C_{NO_2,L}$ are indicated by a series of radiating lines, running from highest to lowest for the cases from HB-LL to HB-HH.), (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying $\alpha \cdot E_{VOCs}$ and E_{NO_x} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. The dashed line indicates the UK air quality standard for hourly NO_2 (105 ppb).

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(a)

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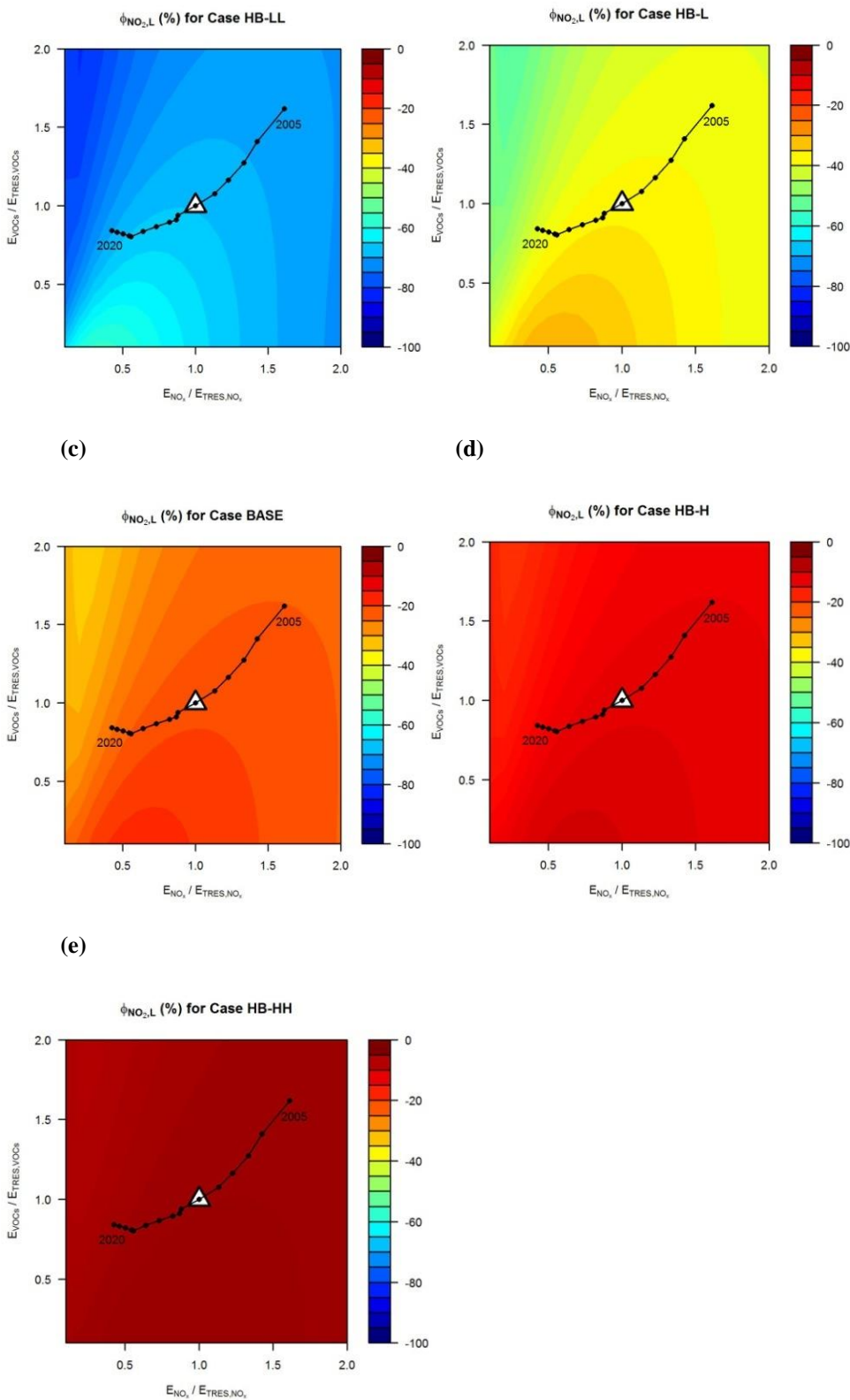
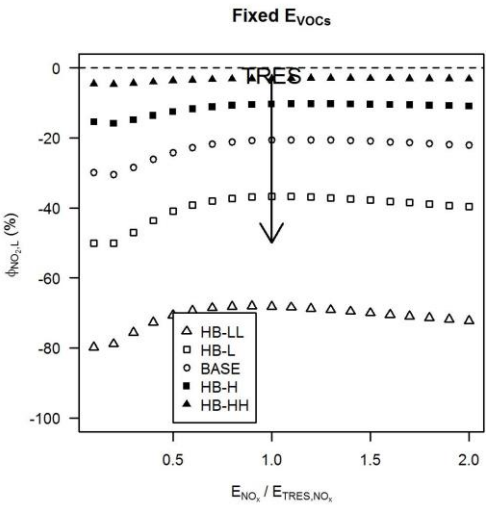
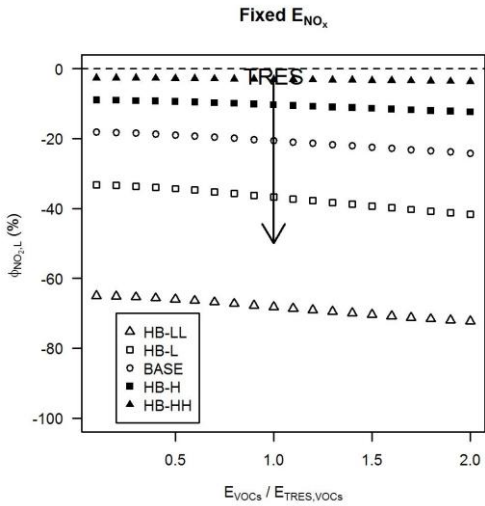


Figure 14 $\phi_{NO_2,L} (\%)$, i.e. the percentage of overestimation for NO₂ in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, in the (a) Case HB-LL ($\alpha = 0.1$), (b) Case HB-L ($\alpha = 0.3$), (c) Case BASE ($\alpha = 0.5$), (d) Case HB-H ($\alpha = 0.7$), and (e) Case HB-HH ($\alpha = 0.9$). E_{VOCs} and E_{NO_x} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010. Trajectory 2005-2020 represents the emission scenarios for 2005 to 2020, assuming constant traffic volume and speed. The solid red curves denote the UK air quality standard for hourly NO₂ (105 ppb).

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(a)

(b)

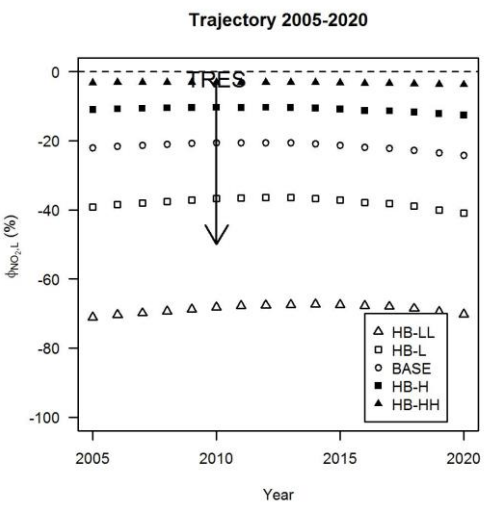
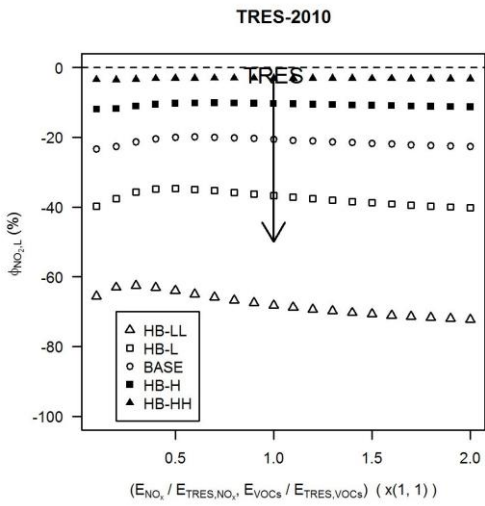


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(c)

(d)



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Figure 15 $\phi_{NO_2,L}$ (%), i.e. the percentage of overestimation for NO_2 in the lower canyon by the ‘one-box’ model compared with that by the “two-box” model, for (a) “Fixed E_{NOx} ” at a fixed NO_x emissions of TRES, (b) “Fixed E_{VOCs} ” at a fixed $VOCs$ emissions of TRES, (c) “TRES-2010” varying the total traffic volume only and (d) “Trajectory 2005-2020” assuming constant traffic volume and speed varying α . E_{VOCs} and E_{NOx} are normalised by those of the Typical Real-world Emission Scenario (TRES, represented by Δ), for the year of 2010.

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